KINETIC MODELLING OF THE HYDROSILYLATION REACTION OF CO_2 USING IRIDIUM (III) COMPLEX CATALYST

BY

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This MSc Thesis is dedicated to Almighty Allah, the Lord of the worlds

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ABSTRACT

Full Name : OLADIPO HABEEBLLAH BOSUN

Thesis Title : Kinetic Modelling of the Hydrosilylation Reaction of CO_2 Using Iridium (III) Complex Catalyst

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The valorization of carbon dioxide, which is a major green-house gas, has been studied in this report. The higher global demand for energy has increased the amount of the carbon dioxide released into the atmosphere from 275 ppm before the industrial revolution to 375 ppm in the year 2000 and 400 ppm in the year 2015. The further increase in the emitted carbon dioxide gave rise to one degree rise in the average temperature of the earth between the year 1960 and 2010 and 0.3 degree rise from 2010 to 2015.

Catalytic CO_2 hydrosilylation is a thermodynamically favored chemical process that could be potentially applied to large-scale transformations of this greenhouse gas. There have been an increasing number of experimental studies during the last decade regarding metal-catalyzed CO_2 hydrosilylation processes. Ruthenium and Iridium catalysts are the first examples of catalytic systems used for CO_2 hydrosilylation. Presently, there are several examples of other catalysts, including transition metal species acting alone or together with $B(C_6F_5)_3$ and organocatalysts which are able to perform this reaction.

In the hydrosilylation reaction, a relatively cheap silicon compound, 1,1,1,3,5,5,5-heptamethyl trisiloxane (HMTS), was catalytically converted to silylformate, which can be hydrolyzed to a

more important compound, i.e. formic acid. The study has focused basically on two type of the Iridium (III) complex type [Ir(H)(CF_3SO_3)(NSiN)(coe)] (Catalyst **1**) and [Ir(H)(CF_3OCO)(NSiN)(coe)] (Catalyst **2**) (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene) for the selective formation of silylformate by solvent free hydrosilylation of CO_2 with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS). The activity of this catalytic system depends on the reaction temperature and the CO_2-pressure. This work includes a kinetic study at variable temperature (from 25 ^oC to 75 ^oC) and pressure (from 1 bar to 8 bar) together with a kinetic modelling of this catalytic reaction. The best catalytic performances have been achieved at 75 ^oC and 8 bar of CO_2.

The Arrhenius equation was used for the kinetic modelling and non-linear regression of the experimental data used in predicting the kinetic parameters i.e. rate constant and the activation energy. The average activation energies estimated for the catalyst **1** and **2** were 72.1 kJ/mol and 47.5 kJ/mol respectively, thereby giving an indication that catalyst **2** is more efficient than catalyst **1**.

الملخص

الاسم الكامل: **أولاديبو حبيب الله بوسن**

عنوان الرسالة: **نمذجة حركية تفاعل الهيدروسايليلاشن لغاز ثاني أكسيد الكربون باستخدام محفزات مركب الاريديوم**

التخصص: **الهندسة الكيميائية**

تاريخ الدرجة العلمية: **يناير 2016**

أن تثمين ثاني أكسيد الكربون، وهو غاز الاحتباس الحراري الرئيسي قد تمت دراسته في هذا التقرير. ان ارتفاع الطلب العالمي على الطاقة قد أدى الى زيادة كمية ثاني أكسيد الكربون المنبعثة في الجو من 275 جزء في المليون قبل الثورة الصناعية إلى 375 جزءا في المليون في عام 2000 و 400 جزء في المليون في عام 2015. حيث أدت هذه الزيادة في ثاني أكسيد الكربون المنبعثة الى ارتفاع درجة واحدة في متوسط درجة حرارة الأرض بين سنة 1960 و 2010 و ارتفاع 0.3 درجة في الفترة من 2010 الى 2015.

يعتبر تفاعل الهيدروسايلاشن لغاز ثاني أكسيد الكربون المحفز عملية كيميائية بفضل الديناميكا الحرارية التي يمكن أن يحتمل تطبيقها على تحولات واسعة النطاق لهذا الغاز المسبب للاحتباس الحراري. هناك عدد متزايد من الدراسات التجريبية خلال العقد الماضي فيما يتعلق بعمليات الهيدروسايليلاشن لغاز ثاني أكسيد الكربون المحفزة معدنياً. محفزات الروثينيوم وإيريديوم هي الأمثلة الأولى من الأنظمة الحفازة المستخدمة في الهيدروسايليلاشن لغاز ثاني أكسيد الكربون. في الوقت الحاضر، هناك العديد من الأمثلة من المحفزات الأخرى، بما في ذلك الأنواع المعدنية الانتقالية التى تتصرف بمفردها أو بالاشتراك مع B (C6F5) 3 و المحفزات العضوية التي هي قادرة على أداء هذا التفاعل.

في تفاعل الهيدروسايلاشن يتم تحويل مركب السيليكون رخيصة نسبيا heptamethyl-1،1،1،3،5،5،5 باستخدام محفز الى سايلوفورمات والتي يمكن أن تحلل إلى مركب أكثر أهمية، أي حمض الفورميك. وقد ركزت الدراسة أساسا على نوعين من مركب الإيريديوم (III)، [$Ir(H)(CF_3SO_3)(NSiN)(coe)$] (محفز 1) و [$Ir(H)(CF_3OCO)(NSiN)(coe)$] (محفز 2) (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene وذلك للتشكيل الانتقائي للسايلوفورمات بتفاعل الهيدروسايليلاشن لغاز ثاني أكسيد الكربون الخالية من المذيبات مع 5،5،5،3،1،1،1-

heptamethyltrisiloxane (HMTS) . نشاط هذا النظام التحفيزي يعتمد على درجة حرارة التفاعل وضغط ثاني أكسيد الكربون. ويشمل هذا العمل دراسة الحركية في درجة حرارة متغيرة (من 25 درجة مئوية إلى 75 درجة مئوية) والضغط (من 1 بار إلى 8 بار) جنبا إلى جنب مع نمذجة حركية هذا التفاعل المحفز. وقد تحقق أفضل أداء تحفيزي في 75 درجة مئوية و ضغط ثاني أكسيد الكربون يعادل 8 بار.

تم استخدام معادلة أرينيوس للنمذجة الحركية وكذلك طريقة الانحدار غير الخطية للبيانات المعملية المستخدمة في التنبؤ بالمعاملات الحركية مثل ثابت معدل وطاقة التنشيط. وجد ان متوسط طاقات التنشيط المقدرة للمحفز 1 و 2 72.1 كيلو جول / مول و 47.5 كج / مول على التوالي، مما يعطي مؤشرا على أن حافز 2 أكثر كفاءة من حافز 1.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The need to reduce the level of the green-house gases in the atmosphere has gained the interest of researcher. This is as a result of the global warming these green-house gases are causing. One of the major green-house gases is carbon dioxide, which is the end product of the fossil fuel combustion. Others include methane, nitrogen (I) oxide, water-vapor and so on.

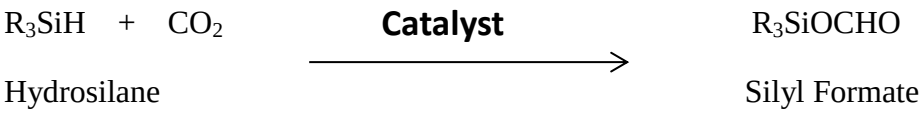
One of the major effects of this green-house gas is the rise in the average temperature of the earth. It has been observed that, between the year 1920 and 1940, there was a 0.5 degree celsius increase in the average temperature of the earth (NASA). Between the year 1960 and 2010, the increment was about 1 degree celsius which was due to higher human activities leading to the emission of carbon dioxide. The consequences of this rise in temperature of the earth surface include rise in sea level, more flooding cases, extremely hot weather in some parts of the world and many more.

The above discussion has led to the focus of many areas of research on the capture of carbon dioxide. Various methods have been devised in order to accomplish this mission. In the Petroleum Engineering research, Carbon Sequestration used in enhanced oil recovery is one of the major ways of dealing with the green-house gas. However, in the Chemical Engineering research, the bio-chemical aspect makes use of the micro-organisms such as cyanobacteria for the carbon capture. Adsorption is another method of capturing carbon dioxide. Various materials

that have the ability of adsorbing carbon dioxide have been developed. This includes the use of activated carbon, lithium zirconate, among others. Fossil fuel, which is the primary source of energy, contributes greatly to the abundance of the green-house gas [1]. Several ways in which carbon dioxide is being captured was also highlighted [1]. Among the various ways highlighted include the use of ocean fertilizer. Ocean is known to be a sink for carbon dioxide. The presence of phytoplankton in the ocean enhances this ability. By adding more nutrients for the phytoplankton in the ocean, an increase in the amount of carbon dioxide being sucked by the ocean will be experienced. However, caution must be taken in employing this method, as a more deadly greenhouse gas, such as methane, could be produced along the line. Other ways highlighted by this reference material include the injection into the ground, and dumping into the ocean. The disadvantage of the former is leakage which eventually leads to the adulteration of the underground water. Another major challenge with this method is the finding of the National Research Council that this could, in the future, lead to earth-quake. Furthermore, the bacteria present in the earth crust may be affected by this method. Therefore, carbon-fixation remains the most viable of capturing the green-house gas and this is the area of research we are focusing. Some reactions that are less important have been studied in the past. These include the conversion of the gas to carbon monoxide. Fixation of carbon dioxide by its conversion to hydrate is another plausible solution to the emission of the gas. In this method, carbon dioxide at high pressure in exposed to water and a hydrate is formed. This hydrate could be used as an alternative source of energy.

An economical way of combatting the abundance of the major green-house gas, which is carbon dioxide, is the valorization of the gas with catalytic reactions like hydrosilylation.

Hydrosilylation reaction is the addition of Si-H bonds (from a hydrosilanes) across unsaturated compounds like alkenes, alkynes, ketones, carbon dioxide etc. Since carbon dioxide has two double bonds linking the two oxygen atoms to the carbon atom, the application of the concept of hydrosilylation can be successfully applied with a suitable catalyst. Although carbon dioxide is thermodynamically unreactive, however, the use of catalyst could transform the gas into valuable products [2]. In the early years of the 80's an insight into the use of the Iridium and Ruthenium complexes as active catalysts for the fixation of Carbon dioxide with silane reagents [3]. In the work, the hydrosilanes were converted to silyl formate with the use of Ruthenium phosphine complexes as the catalyst.



The hydrosilane starting materials are cheap, easy to handle, readily available and environmentally harmless compounds. CO_2 hydrosilylation represents a thermodynamically favorable process for the transformation of CO_2 into value added chemicals such as silyl formates. Different types of silylformates are formed depending on the type of hydrosilane used. This CO_2 valorization method allows production of silylformates which have been used as C1 building blocks in the synthesis of methane [4] [5], formic acid [4] [6], formamides [5] and amines [7].

1.2 PROBLEM STATEMENT

The conventional formation of formic acid from carbon dioxide and hydrogen is thermodynamically unfavorable, with a positive ΔG. Therefore, very high pressure is required

for this process [6]. A later advancement in the C1 building blocks was the catalytic hydrosilylation reaction, which requires lower CO_2 pressure.

This research work makes use of 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS), which is a member of the hydrosilane homologous series with oxygen atoms in the silicon backbone forming the (O-Si-O) bond, as the starting material. HMTS is a colourless liquid at room temperature and has a boiling point of 142 ^{o}C. Siloxanes are derived from the condensation reaction of two silanols which are analogous to alcohol but with the carbon backbone replaced with silicon. The catalytic reaction of the HMTS with CO_2 affords the corresponding silyl formate which can be hydrolyzed into formic acid.

1.3 RESEARCH CONTRIBUTION

Before the Industrial Revolution in 1750, the level of carbon dioxide was about 275 ppm (NASA) and the natural cycle was maintained. However, the level increased to 375 ppm, which is about 40% increment, in the year 2000. This is due to the human activities added to the natural source of carbon-dioxide. These activities include, but not limited to, deforestation, emissions from industrial stacks and electricity supply. Coupled with the human activities, the rapid growth of the world population in the 20th century has increased the demand for more deforestation. This has also led to the increase in the amount of carbon dioxide excreted by humans. Photosynthesis, which is the most important natural phenomenon of capturing carbon dioxide, has decreased in level due to the deforestation.

In this research, we made use of a chemical compound, of less value, to capture the carbon dioxide, thereby adding more value to the compound. As previously mentioned, 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) was used as our starting material and converted to silyl formate

in the presence of carbon dioxide and Iridium (III) complex catalyst. The conversion of CO_2 into silyl formate is an important step for the formation of several compounds like methane [4] [5], formic acid [4] [6], formamide [8] and amines [7].

Formic acid is a colourless compound with pungent smell and occurs naturally in ant or bee stings. It is however produced industrially from the hydrolysis of the product of the reaction between methanol and carbon monoxide (methyl formate) with methanol as the by-product. An old method of production is by reacting sodium formate with a mineral acid. Other industrial ways of production include the hydrolysis of formamide, the oxidation of hydrocarbons such as butane and naphta. Formic acid has various uses ranging from food preservatives to medical treatment use. It is also an important intermediate in chemical synthesis. It is used as a coagulating agent in rubber production. Other uses of formic acid include the promotion of fermentation, addition to poultry feed to serve as anti-bacteria such as E.colli. It costs between 850 to 1,200 USD per tonne in the United States and it's largely produced in Germany.

The formamide, which is also one of the derivatives of silylformate, is a colourless liquid with a smell similar to that of ammonia. It is used in the agriculture sector either as a pesticide or an herbicide. In the pharmaceutical sector, it is used in the manufacture of certain drugs. Due to the presence of Nitrogen in the compound, it is used as a polar solvent. It can be produced by the reacting the silyl formate formed with ammonia. It is produced industrially by reacting carbon monoxide with ammonia. It is also produced by subsequently reacting ammonia with methyl formate formed from the reaction of carbon monoxide with methanol.

Historically, formamide is produced from the reaction of ethyl formate and ammonia or from the reaction between ammonia and formic acid. The later produces ammonium formate which is subsequently heated to give formamide and water vapor.

Another important derivative of the silylformate is the polymeric compounds of silicon known as silicone. They have desirable qualities such as resistance to heat and rubber-like properties, thereby giving them various applications. They are used as coating for electrical wires, handles for kitchen appliances, car radiator gaskets and so on. Silicon based polymers can be linear, branched and network and other forms which the polymers of carbon exist. The Si-O bond gives silicones preferential properties over the polymers formed with only carbon in the backbone or those with C-O in the polymer backbone. The flexibility of the bond is responsible for the lower T_g of silicones. It is also responsible for the flexible nature of the silicones.

The derivatives obtainable from silylformate have been shown to have various applications. The demand for formic acid in the animal feeds surpasses demand from any other area of application of the acid. This is due to the high consumption of meat in the world. In the year 2013, the global demand for formic acid was 579,000 tons per year and the highest consumer was Asia Pacific having a demand of 294,000 tons per year. However, the production level was at 697,000 tons per year in the same year. These are represented in the bar chart below in figures 1 and 2. It is expected that the demand will rise to 690,000 tons per year in 2018 with a 3.6% yearly rise. Of the different purity levels available in the market, the 85% purity level is the most widely utilized. The price of the chemical depends on the purity level and varies from a location to the other. For a purity level of 85%, it was sold in the year 2014 at 1$/kg in the Europe and 0.86$/kg in the United States. As mentioned earlier, the highest producer is BASF in Germany with a capacity of 180,000 tons per year.

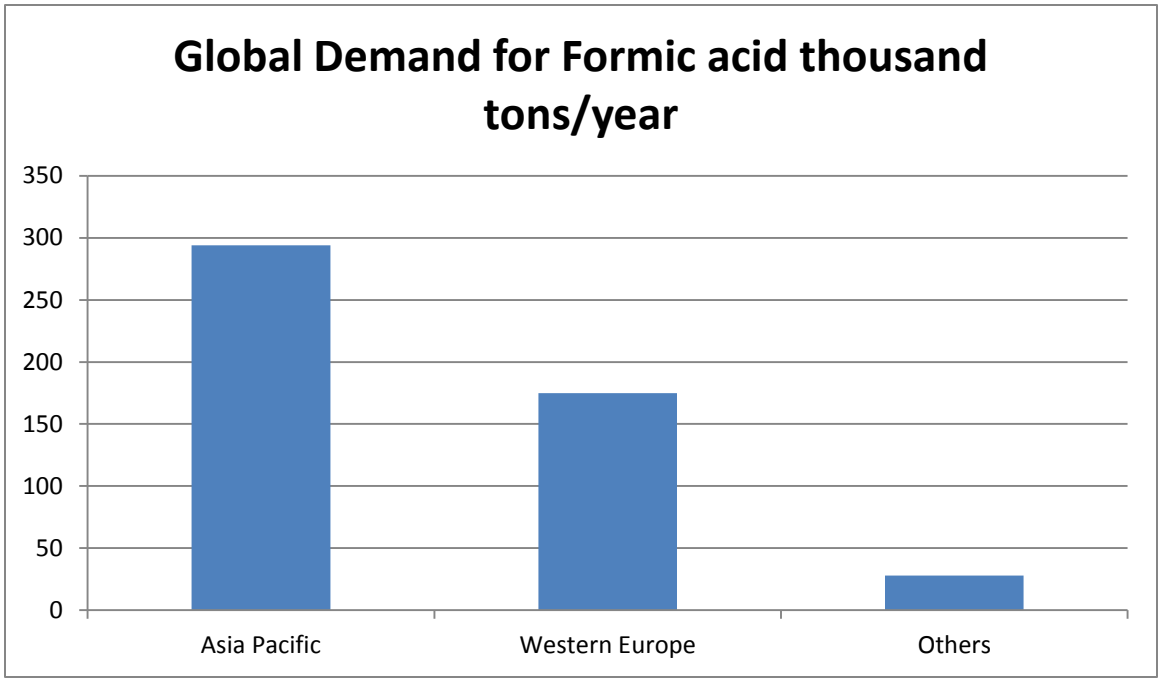


Figure 1: Global demand for formic acid per year

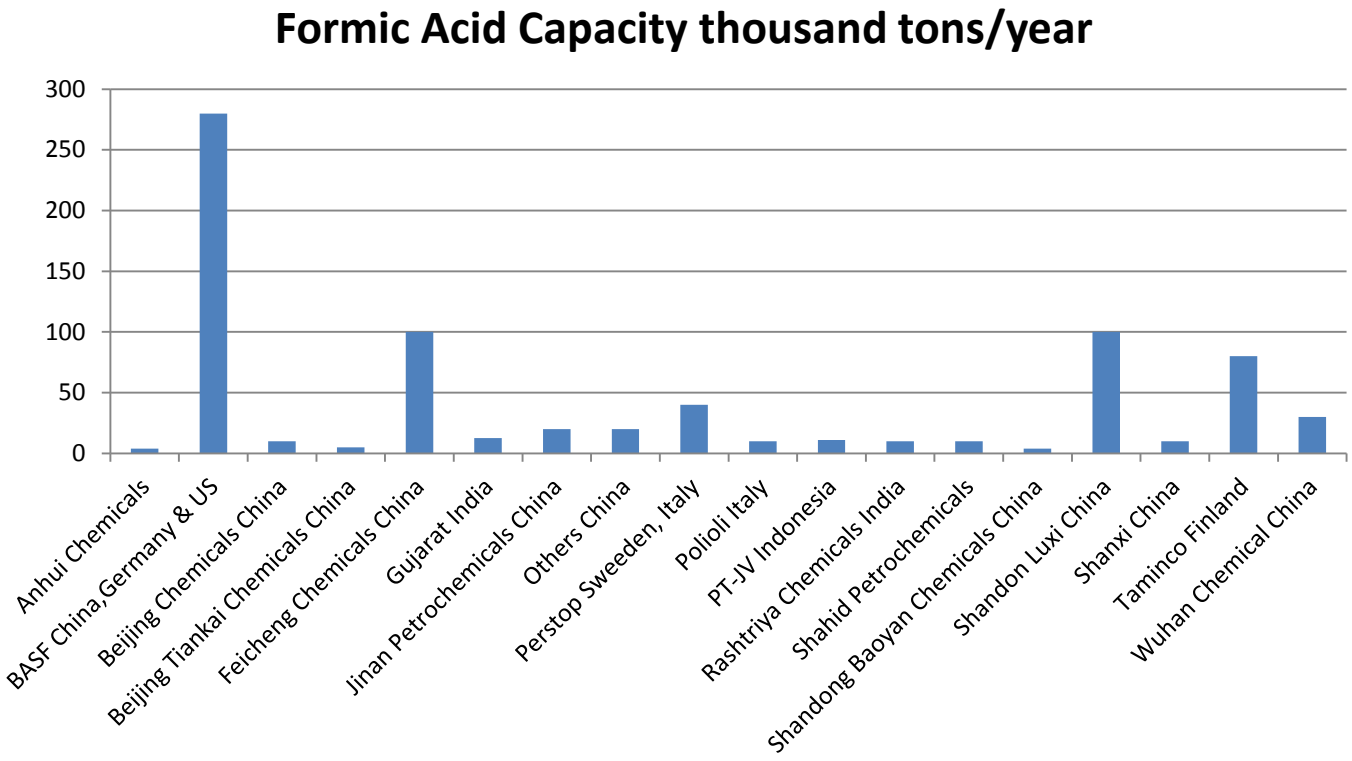


Figure 2: Formic acid capacity per year

Out of the three derivatives of the formate mentioned, the silicones are the most highly demanded. It is expected that by the year 2019, the demand would have risen to $19.6 billion. This figure results from a yearly increasing rate of 5.8% per year of the polymer. The highest demand comes from the Asia Pacific followed by Africa/Middle East. The high demand in the Asia Pacific can be attributed to China which accounts for as much as 60% consumption in the region. Among the various areas of application, the electrical/electronic segment receives the highest demand. Next is the construction industry, however, the story will turn around through the year 2019 with construction contributing highest to the demand for silicone.

1.4 THESIS OBJECTIVE

This research focusses on the transformation of a relatively cheap siloxane compound (specifically 1,1,1,3,5,5,5-hexamethyl trisiloxane) into silyl formate which serves as the reagent for the formation of value-added products like formic acid, formamide and silicones. There is a need to synthesize a catalyst for this reaction and observe the activity of this catalyst. The selectivity of the catalyst for silyl formate is a very important consideration when synthesizing the catalyst due to the possible reaction between the silyl formate formed and HMTS. An organo-metallic catalyst, iridium complex, is employed for this transformation of the green-house gas, CO_2 into more important products. The specific Iridium-complex catalysts used are Ir(H)(CF_3SO_3)(NSiN)(coe) (Catalyst **1**) and Ir(H)(CF_3OCO)(NSiN)(coe) (Catalyst **2**), where NSiN is bis(pyridine-2-yloxy)methylsilyl and coe is cyclooctene.

1.4.1 SPECIFIC OBJECTIVES

- Investigate the transformation of CO_2 into valuable product(s) using Iridium based homogeneous catalysts

- Study the effects of different ligands in the Iridium catalysts on the activity of the reaction
- Study the effect of Temperature and Pressure on the activity of the reaction
- Study the kinetics of the CO_2 hydrosilylation to calculate the Activation energy

CHAPTER 2

LITERATURE REVIEW

Quite a number of researchers have worked on the ways to reduce the level of the greenhouse gases (especially carbon dioxide) in the environment. Oro and co-workers described several catalytic hydrosilylation of CO_2 in recent review [9]. In general, Iridium, Rhodium, and Ruthenium complexes are used as the catalyst for this reaction when talking about transition metals. A lewis acid $B(C_6F_5)_3$ together with transition metals or frustrated lewis pairs also acts as an acid catalyst for hysdrosilylation reaction [10]. The third category involves the lewis base that are metal-free, such as carbine [11]. Riduan and co-workers concluded that these processes can be done on a large scale because of its thermodynamic feasibility.

Recently, research trend in the area of carbon capture has been on how to convert carbon dioxide into a value added product (such as esters, fuels and some other highly important compounds) rather than just capturing it and laying it fallow. In the following sections, several hydrosilylation reactions are classified based on the valuable products resulting from each.

2.1 ESTER PRODUCTION

The production of the ester of formic acid by the hydrosilylation reaction has gained the interest of researchers in recent years. Various catalysts are utilized for this purpose and they include the ruthenium, copper (I) N-heterocyclic carbine, rhodium and iridium.

2.1.1 RUTHENIUM COMPLEX CATALYSIS

The catalytic conversion of hydrosilane into the corresponding esters was first reported in the year 1981 using the ruthenium complex as the catalyst by Suss-fink and Reinner [12]. They made use of $[HRu_3(CO)_{11}]^-$ for the conversion of triethyl hydrosilanes into triethyl silylformate. This hydrosilylation reaction proceeded under a high temperature and pressure (T = 60 ^oC and P_{CO2} = 60 bar). 61% of the triethyl hydrosilane starting material was converted into several products which include Et_3SiOH, $Et_3SiOSiEt_3$ and $Et_3SiOCHO$ with the yield of the desired product 81%.

Jansen and co-worker used the ruthenium (III) and ruthenium (II) complexes for the catalytic conversion of n-Hex_3SiH, Me_2PhSiH, Et_2SiH_2, Ph_2SiH_2, and p-C_6H_4-$(Me_2SiH)_2$ into their various silyl formates [13]. The reaction rate was found to generally increase with the reaction temperature. When Me_2PhSiH was used as the substrate, the reaction did not proceed until the temperature was increased above 40 ^oC. It was also concluded that the yield of the desired silyl formate improves as the temperature of the reaction is increased.

2.1.2 Cu (I) NHC CATALYSIS

The copper (I) N-Heterocyclic Cerbene was used to catalyze the carbon dioxide hydrosilylation reaction by Zhang and co-worker [14]. The hydrosilane used was $(EtO)_3SiH$ and the reaction proceeded under a very mild condition (1 bar CO_2 pressure and temperature from 20 to 100 ^oC) with a yield of up to 71% for the silyl formate achieved. The best catalytic activity was at a reaction temperature of 100 ^oC, with 99% conversion of the $(EtO)_3SiH$ starting material. The reaction step was confirmed by the characterization of a copper formate as an intermediate in the reaction thereby giving an insight into the reaction mechanism that the hydrosilane initiated the attack.

2.1.3 RHODIUM COMPLEX CATALYSIS

The rhodium complex together with inorganic base was used for the hydrosilylation reaction of carbon dioxide [15]. Itagaki *et al.* used various combinations of rhodium complex and bases (K_2CO_3, Cs_2CO_3, K_3PO_4, Et_3N and without any base). The best reaction condition was when K_2CO_3 and Cs_2CO_3 was used in combination with $Rh_2(OAc)_4$ (OAc=Acetate) while no reaction occurred when the base metal was absent. The starting material, dimethyl phenylsilane was totally consumed (>99% conversion) within 2 hrs. The reaction proceeded under mild reaction condition (1 bar of CO_2 and temp=50 ^oC). The yield for the reaction was up to 90% and depends on the

2.1.4 IRIDIUM COMPLEX CATALYSIS

The first iridium complex used for the hydrosilylation reaction of CO_2 into silyl formate was the Ir(CN)(CO)dppe, [dppe=1,2-bis(diphenylphosphino) ethane] [16]. The hydrosilanes used for the transformation was trimethyl hydrosilanes and the CO_2 pressure was 1 atm with the reaction temperature of 25 ^oC. However, the silyl formate formed was unstable and quickly converted into methoxide with little formate remaining after equilibrium is reached.

A more selective iridium catalyst for the formation of the formate was the [Ir(H)(CF_3SO_3)(NSiN)(coe)] used for the CO_2 hydrosilylation of 1,1,1,3,5,5,5-hexamethyl trisiloxane [17]. The reaction was performed at room temperature and the CO_2 pressure was 3 bar. The yield of the formate was as high as 90% and all the siloxane was totally consumed. The study also poses an advantage of solvent-free catalysed reaction which gives a more environmentally friendly process. Matokura and co-workers [18] recently reported the hydrosilylation of polymethyl hydrosiloxane with a high yield of silyl formate (91%) but in 1,4-

dioxane solvent which is a volatile organic compound. This will have an environmental hazard when the process is industrialized.

For all the catalytic hydrosilylation reactions, the kinetic studies for the determination of the rate constants and the activation energies have not been explored. This thesis focusses on the estimation of this kinetic parameters and the study of the effect of pressure of CO_2 on the kinetic parameters. The work of Oro and co-workers [17] has been extended in this study.

2.2 PRODUCTION OF FUEL FROM CARBON DIOXIDE

Some other ways of capturing the gas include the conversion of the green-house gas into various fuels and fuel additives. Among the various fuels obtainable from carbon dioxide are methane, methanol and hydrogen, while the fuel additives derivable from carbon dioxide are dimethyl carbonate while formic acid is a potential fuel substrate.

2.2.1 METHANE PRODUCTION

Matsuo *et. al.* studied the catalytic reduction of carbon dioxide with the aid of an hydrosilanes. The final product of the reaction was methane with silyl acetal as the intermediate. Siloxane by-product was also formed in the reaction. The catalyst utilized for this reaction was a mixture of zirconium benzyl-phenoxide complex and $B(C_6F_5)_3$. The mixture of tris(pentafluorophenyl)-borane and mono-, bi-, or tri-dentate ligands of the zirconium complex catalysts were used for the reaction of CO_2 and dimethyl phenyl hydrosilane and the activity of the catalysts compared. 15, 19 and 98% yields were obtained respectively after 1.5 hour of reaction. This gave the tri-dentate ligand the catalyst with the highest activity for the production of methane from the particular substrate utilized. Park and co-workers tried both bulky ligand and less bulky group and found out that the use of a less bulky group gave more methane than using bulky group as

the ligand [4]. Furthermore, there was an intermediate compound formed along the line but not visible. This intermediate compound is the formate which is then finally converted to siloxane and methane.

2.2.2 METHANOL PRODUCTION

Methanol was also synthesized from the catalytic hydrogenation of carbon dioxide in the presence of Cu-ZnO as the catalyst [19]. When the catalyst was changed to Zn/Cu-ZrO_2 a better selectivity of methanol was realized. The finding of this work was that ZrO_2 is responsible for the selectivity of methanol in the reaction, whereas, ZnO increases the surface area leading to a well dispersed Cu at lower temperature and therefore a better catalyst activity observed. Apart from the fact that a very dangerous gas, CO, is produced from the reaction, the reaction only proceeded with a reasonable yield at a high temperature (247 ^{o}C) and pressure (9 bar).

The effect of the addition of zirconia on the hydrogenation reaction of CO_2 to methanol was studied and a positive response observed. The rate of reaction was found to increased with increase in the addition of zirconia [20]. It was further observed that the effect is more pronounced in the case of CO to methanol than that of CO_2. Furthermore, the reaction path for the CO to methanol was changed with the addition of zirconia and this was reflected by the decrease in the activation energy for this reaction, whereas, in the case of the CO_2 to methanol, the activation energy was not changed significantly. This observations are explained by a reaction mechanism of dissociative adsorption of hydrogen in the case of Cu/SiO_2 catalyst while adsorption of CO and CO_2 in the case of addition of zirconia.

Another way of converting the CO_2 into methanol fuel using a metal-free catalyst is the use of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as the catalyst and the hydrogen source was an

hydroborane, specifically, 9-borabicyclo[3.3.1] nonane [21]. This was the first Nitrogen-base catalyst used for the hydrogenation reaction. $HCOOBR_2$ formate and $H_2C(OBR_2)_2$ acetal were the intermediates formed in the reaction.

2.2.3 CLEAN FUEL PRODUCTION

The main product of the combustion of Hydrogen is water which is eco-friendly. Therefore, hydrogen is generally referred to as a clean fuel. Apart from the various methods of production of hydrogen, it can also be produced from carbon dioxide under appropriate conditions.

The production of synthetic gas ($CO + H_2$) from carbon dioxide was investigated by Lehn and co-workers [22]. This reaction is very similar to the natural photosynthesis where carbon dioxide and water are converted into glucose in the presence of sunlight. In this artificial photosynthesis which converts carbon dioxide into carbon monoxide and hydrogen, visible light is used as the source of radiation to activate the reactants. Depending on the presence of certain chemicals in the reaction mixture (tri-ethanol amine and bipyridine), selectivity for either carbon monoxide or hydrogen was achieved respectively.

In a reaction that was catalyzed by sunlight/mercury light [23], the production of hydrogen from water and carbon dioxide was also realized by the use of anatase titania (the photocatalyst) and ZnO/Cu (the electrocatalyst). The effectiveness of this material (thin film of anatase titania) was compared with rutile and the result reveals that the former has an higher efficiency over the latter.

2.3 OLEFIN PRODUCTION

Another important area where value is being added to CO_2 is in the conversion of the gas to hydrocarbons by its hydrogenation [24]. Aluminium oxide precipitated with Magnesium oxide

was used as the catalyst support for the reaction. The active site was iron promoted with potassium. Depending on the fraction of MgO present in the catalyst, selectivity for olefins (ethylene to butene) and C_5 hydrocarbon varied. With up to 0.2 weight fraction of MgO, selectivity for the above hydrocarbons was observed.

In a similar reaction, selectivity for olefins (ethylene to butene) and C_5 was observed to be dependent on the group-one metals present in the catalyst as catalyst support [25]. Various group-one metals were used as support starting with Lithium and Sodium. Other group-one metals used were Potassium and Rubidium. Rubidium gave the best selectivity for the olefins followed by Potassium. This was linked to the increase in the basicity of the surface of the catalyst and this has effect on the selectivity of the catalyst. It was concluded that selectivity for the olefins increases as we go down the group of the alkali metals.

2.4 PRODUCTION OF CARBONATES AND METHOXIDE

The use of carbon dioxide in the production of dimethyl carbonate is another area where the green-house gas is being utilized for valuable products. Exploration of the reaction between methanol and carbon dioxide to give dimethyl carbonate has been done by several researchers with most of the reactions involving the use of Cerium catalyst [15], [26], [27]. Dimethyl carbonate has found various applications including the use as fuel additive and also in producing polymer (that is polycarbonate).

The conversion of CO_2 into dimethyl carbonate was catalytically achieved by the use of cerium oxide [26]. One of the challenges of this reaction is its reversibility nature. Since the reaction produces water as a by-product, its removal from the reaction mixture will give a higher yield of the dimethyl carbonate. Honda *et. al.* made use of 2-cyano pyridine as the dehydrating agent for

the reaction. After complete hydration of 2-cyano pyridine, 2-picolinamide is formed which can easily be recycled in a reaction catalyzed by Na_2O/SiO_2.

The comparison of the effect of cerium oxide catalyst and copper-cerium oxide catalyst on the reaction of CO_2 with ethanol to form dimethyl carbonate has also been reported [27]. At 0.1wt% copper in the catalyst and temperature of 393 K and 1.3 MPa pressure, the highest conversion rate was reported. Any further increase in the amount of copper in the catalyst leads to a decrease in the reaction rate. The reason for this occurrence was the covering of the active sites of the catalyst when the proportion of copper exceeds this threshold value. The increase in the reaction rate due to copper addition to the catalyst was attributed to the speeding up of the reduction of Ce^{4+} to Ce^{3+} when copper was added. This effectiveness of copper was also linked to the reduction of the defect sites when copper-cerium oxide was used as the catalyst.

In the hydroboration of CO_2, nickel complex was used for the catalytic conversion of CO_2 into methoxide which was reported by Chakraborty *et. al.* [28]. This reaction requires less energy and proceeded at room temperature in borane medium.

CHAPTER 3

EXPERIMENTAL

3.1 EXPERIMENTAL SET-UP

The iridium (III) complex catalyzed hydrosilylation reaction between 1,1,1,3,5,5,5-heptamethyl trisiloxane (HMTS) and carbon dioxide was carried out in a system capable of excluding air. For the proper exclusion of air in the reagents used for the reaction, both MB-UNILAB glove box (Figure 3) and Sclenk technique (Figure 4) were used to store the catalyst and chemical reagents respectively. In the Schlenk tube (Figure 4), both vacuum pump and Nitrogen cylinders were connected in order to ensure an inert atmosphere. The HMTS and THF, solvent for GC-MS sample preparation were stored under this condition in the Schlenk tube while the catalyst was stored inside the glove box. For the reaction, a well-insulated batch reactor of volume 25 ml and Teflon-lined was also utilized as shown in Figure 5. The carbon dioxide gas in cylinder with a purity level of 99.99% was purchased from a commercial source and utilized for the reaction. The batch reactor is connected with temperature and stirrer controller. The reactor inlet is connected with the CO_2 gas cylinder and outlet is connected with vacuum. Samples were collected through sample withdrawing valve.

Figure 3: The glove box

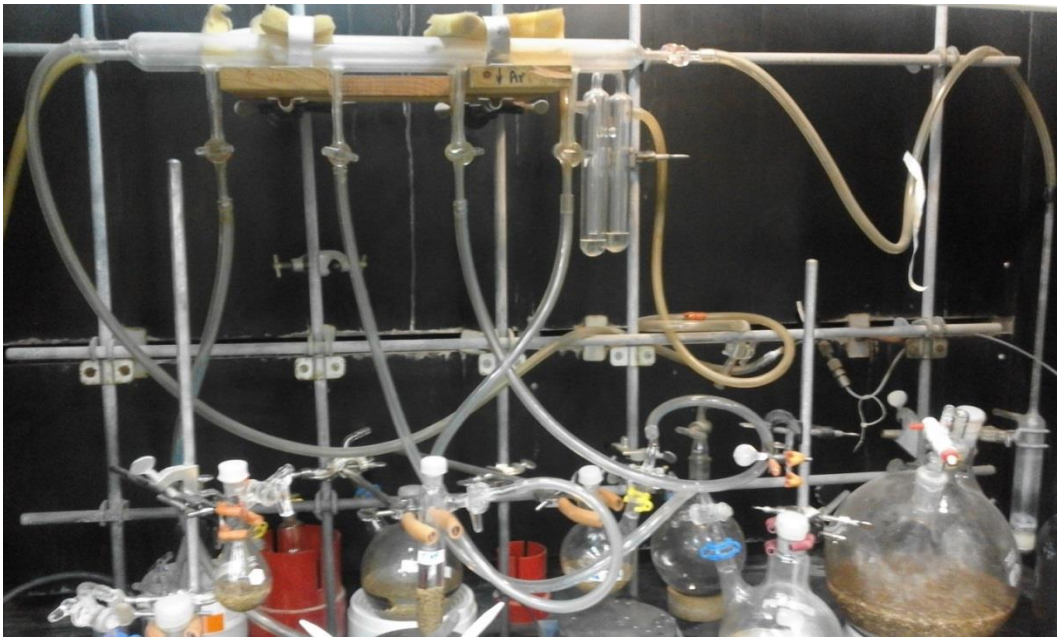


Figure 4: The schlenk tube

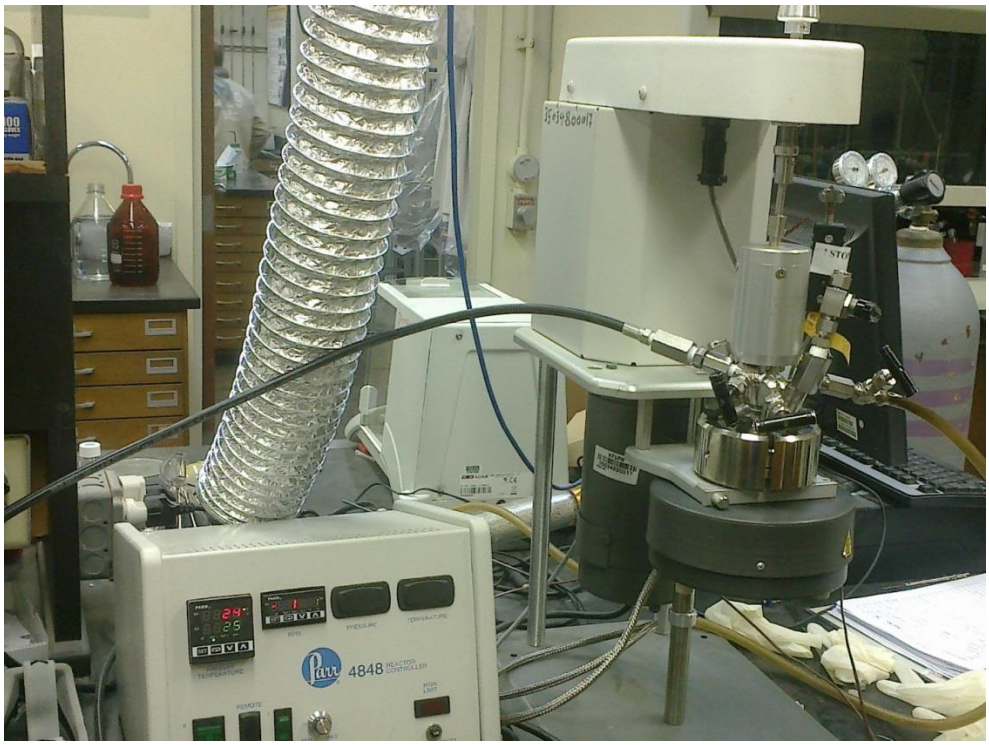
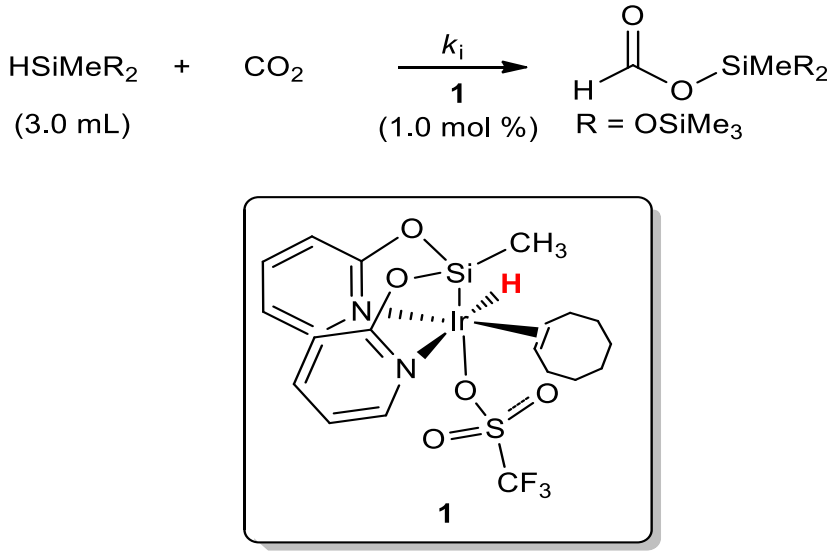


Figure 5: Batch reactor used for the hydrosilylation reaction

PROCEDURE FOR CATALYTIC HYDROSILYLATION REACTION

A 25 ml batch reactor with Teflon lining inside was charged with dry HMTS [HSiMe(OSiMe3)2] (3 mL,11.04 mmol). Then the reactor was closed, purged with CO_2 gas few times and heated to the corresponding temperature. After stabilization to the corresponding temperature and CO_2 pressure, the reactor was opened under argon atmosphere and the iridium catalyst **1** (75 mg, 0.11 mmol), which was weighed in a glove box, was added. After closing the reactor, the system was purged few times using vacuum and CO_2 gas. Then the pressure of CO_2 gas was adjusted to the corresponding value. The reaction mixture was stirred with mechanical stirrer. The liquid samples were taken periodically after releasing the CO_2 pressure, without opening the reactor, using a long needle through sample withdrawal valve. The reactor was

purged with vacuum and CO_2 few times after each sample withdrawal and the pressure was returned back to the desired value bar using CO_2.



Scheme 1: Equation of Reaction

The effect of the carbon dioxide pressure on the selectivity and the activation energy was studied with both Iridium complexes used for the reaction that is [Ir(H)(CF_3SO_3)(NSiN)(coe)] (**1**) (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene) and [Ir(H)($OCOCF_3$)(NSiN)(coe)] (**2**) (NSiN = bis(pyridine-2-yloxy)methylsilyl, coe = cyclooctene). With a constant volume of HMTS, different pressure of 1, 3, 6 and 8 bar pressure of the carbon dioxide gas were used for the reaction and the conversion of HMTS to silyl formate. The temperature was also changed for each CO_2 pressure and for each catalyst between 25 ^oC and 75 ^oC. The decomposition of the catalyst at a temperature above 85 ^oC limited our temperature variation to 75 ^oC.

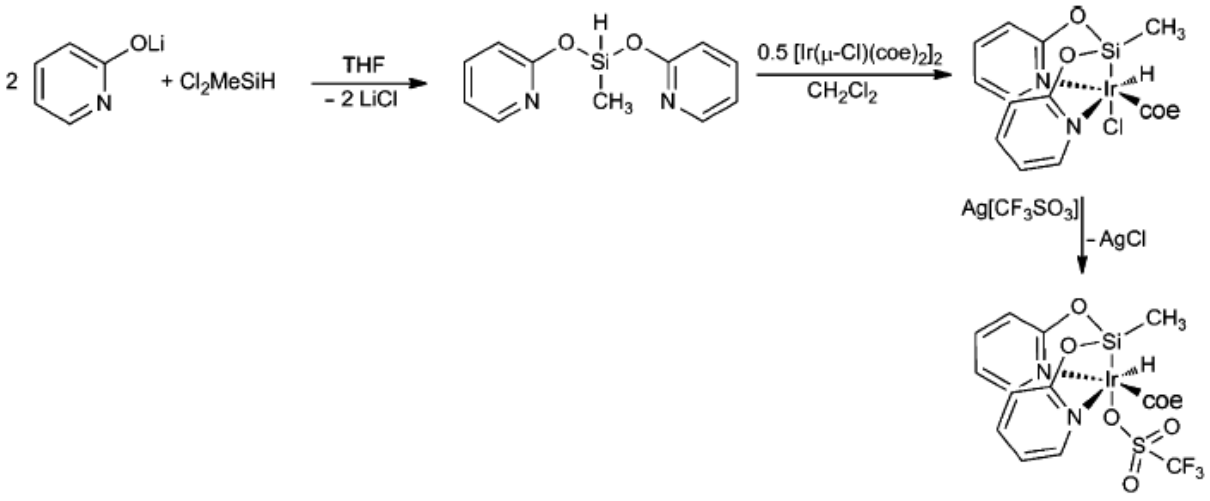
3.2 GENERAL INFORMATION

All experiments were performed with rigorous exclusion of air at an argon/vacuum manifold using standard Schlenk-tube techniques or in a dry-box (MB-UNILAB). The catalytic experi-

ments were carried out using a 25 mL batch reactor with Teflon lining inside. Gas chromatography–mass spectrometry (GC–MS) analyses were performed using Agilent 7890A GC system and Agilent 5975C inert MSD with Triple-Axis Detector MS system with DB1 capillary column (30 m x 250 mm, film thickness 0.25µm). Oven parameters: initial temperature, 80 ^{o}C hold for 3.0 min, then increase the temperature up to 160 ^{o}C by heating rate of 5.0 ^{o}C min $^{-1}$ hold for 1.0 min. Again heated up to 250 ^{o}C by rate of 5.0 ^{o}C min $^{-}$1. Carrier gas flow was 1.8 mL min^{-}1 and injection volume was 0.1 ml. Inlet temperature was 250 ^{o}C and split ratio is 100:1. The iridium(III) complex **1** was prepared according to method reported in the literature [17]. $HSiMe(OSiMe_3)_2$, THF and carbon dioxide (99.99% purity) were purchased from commercial sources. $HSiMe(OSiMe_3)_2$ was dried over 4A molecular sieves previously to use.

3.2.1 CATALYST SYNTHESIS

A brief description of how the catalyst was synthesized will be described in this section. The catalyst preparation passed through different stages with lots of intermediates. The following steps summarize the different stages and processes for the synthesis.



Scheme 2: Synthesis of catalyst precursor

1. The first step is the preparation of bis-(2-(oxy)-pyridine) methylsilane from n-butyllithium and 2-hydroxypyridine. A dropwise addition of n-butyllithium dissolved in hexane to 2-hydroxypyridine dissolved in tetra-hydrofuran (THF) was done in order to produce the desired bis-(pyridine-2-yloxy) methyl silane. The concentrations of the reagents used are 1.6mol/dm^3 and 0.175 mol/dm^3 respectively. The reaction temperature was -78 ^oC. After the reaction, the reaction mixture was taken to the room temperature and stirred. Then the solvent evaporated with vacuum and the left-over washed with hexane before being dissolved in THF. The resulting suspension is then returned to -78^oC. A solution of dichloro-silane in THF with a concentration of 0.53mol/dm^3 was then added in drop to the suspension and stirred continuously. After proper stirring, the solvent was evaporated again with vacuum and washed with hexane. A colorless liquid was then formed after removing the hexane.
2. The next step is the preparation of Ir(H)(coe)Cl(NSiN) from bis-(2-(oxy)-pyridine) methyl silane and $[Ir(\mu\text{-}Cl)(coe)]_2$, where (coe) represents cyclo-octene. A solution of the two compounds in dichloromethane with a concentration of 0.187mol/dm^3 was prepared at the room temperature and stirred for 18 hours. The solvent was then removed with vacuum before washing the residue with hexane.
3. A solution of the compound formed in step 2 was prepared in dichloromethane by dissolving 0.4g of the compound in 12 ml of dichloromethane. Prior to the addition of dichloromethane, 0.2g of Silver triflate was mixed with 0.4g of Ir(H)(coe)Cl(NSiN) and light-protected. The resulting mixture was filtered and the solvent evaporated with vacuum before washing with hexane. Then, the resulting solid was recrystallized with

dichloromethane. The resulting compound has the chemical formula Ir(H)(coe)(OTf)(NSiN) (catalyst **1**). If silver trifluoroacetate is used instead of silver triflate, the catalyst **2** [Ir(H)(CF_3OCO)(NSiN)(coe)] will be obtained.

The complex formed in step 3 was utilized as the catalyst for the hydrosilylation reaction. It should be noted that all the reactions described above were performed either in the Schlenk tube or inside glove box. The chemical structures of the catalysts are as shown in figures 6 and 7.

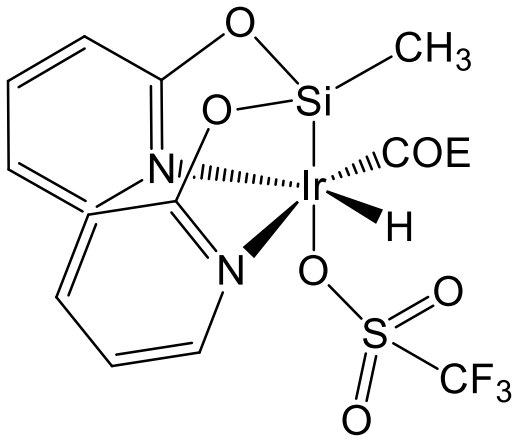


Figure 6: Chemical structure of catalyst **1**

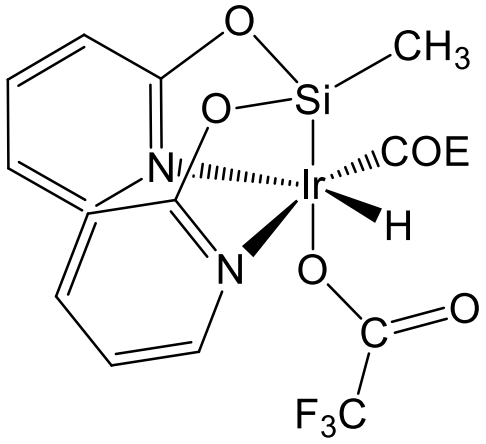


Figure 7: Chemical structure of catalyst **2**

3.3 CHARACTERIZATION OF REACTION SAMPLE

3.3.1 GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

The GC-MS consists of two distinct units; the Gas Chromatography and Mass Spectrometer. The gas chromatography is responsible for the separation of the reaction mixture into its constituent components. The GC-MS used for the analysis has an auto-sampler which automatically takes the sample from the vial and injects it into the column of the GC as shown in Figure 8.

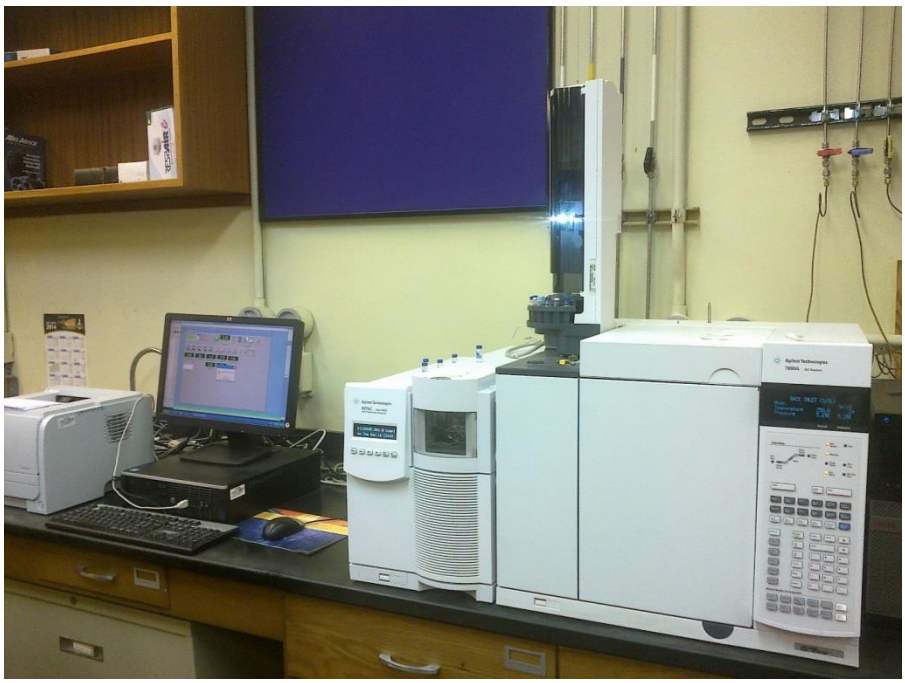


Figure 8: The gas chromatography-mass spectrometry (GC-MS)

After the injection of the sample, the sample is transported with the aid of the carrier gas through the stationary phase, that is, a long and tiny column, where each of the components of the mixture reacts differently with the coating of the coil. The separation of the constituents is actually based on the difference in their boiling point. Components with lower boiling points tend to travel faster with the aid of the helium carrier gas in the column than those with higher

boiling points. The carrier gas serves the purpose of the transportation of the sample components through the column. After the separation of the sample into its different components, the components are then passed to the Mass Spectrometer for both qualitative and quantitative analysis (figures 9, 10 and 11).

In the mass spectrometer, the separated compounds are ionized by bombardment with electrons from the electron gun. The bombardment leads to the fragmentation of the molecules into different positively charged ions (figures 12 and 13). By comparing the fragments with the database of compound fragments, the specific compound is identified. The area of the different peaks detected by the MS is directly proportional to the mass of the constituent molecule in the sample. Therefore, our reaction mixture is correctly quantified and the different components identified.

The reaction sample were collected and diluted in dry tetrahydrofuran (0.5 ml) and analyzed by quantifiable Gas Chromatography-Mass Spectrometry (GC-MS). The product yield was obtained by comparison of the area corresponding to the peaks assigned to the reaction products that corresponding to $HSiMe(OSiMe_3)_2$. The sample collection was continued until the HMTS consumption is completed. The retention time for HMTS is 4.58 min, for silylformate 9.229 min, for $\{(Me_3SiO)_2MeSi\}_2O$ 19.796 min and for formic acid is 1.361 min.

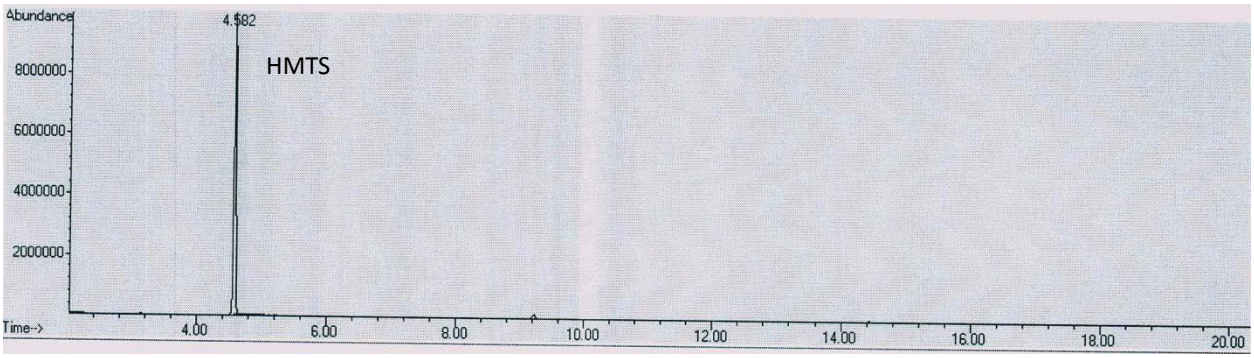


Figure 9: GC spectrum at the beginning of the reactions (HMTS = 100%).

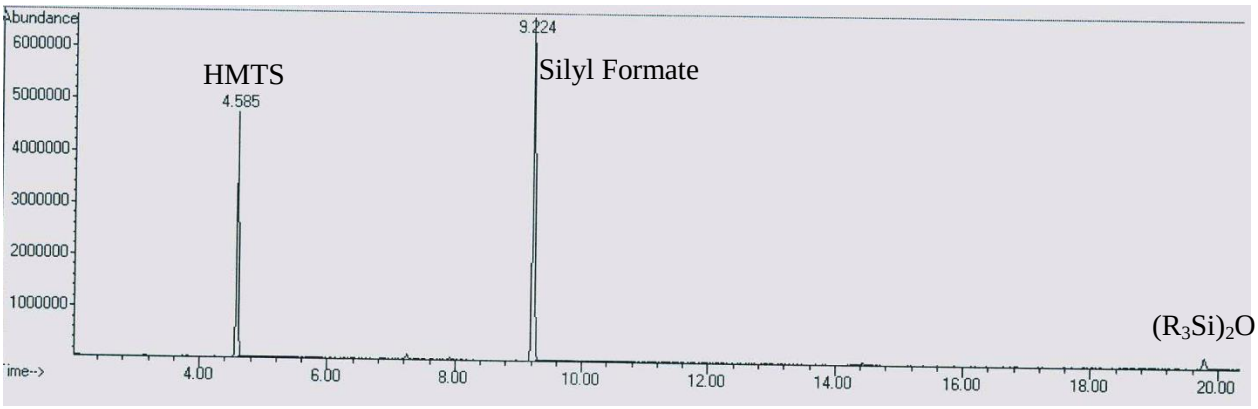


Figure 10: GC spectrum after 2hr (HMTS = 39%, Silyl Formate = 59%)

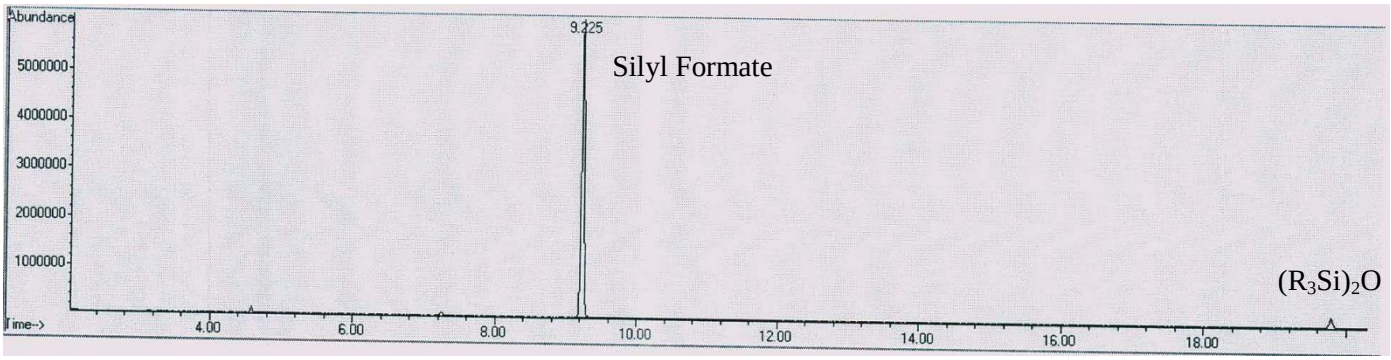


Figure 11: GC spectrum at the end of the reaction (Silyl Formate = 95%)

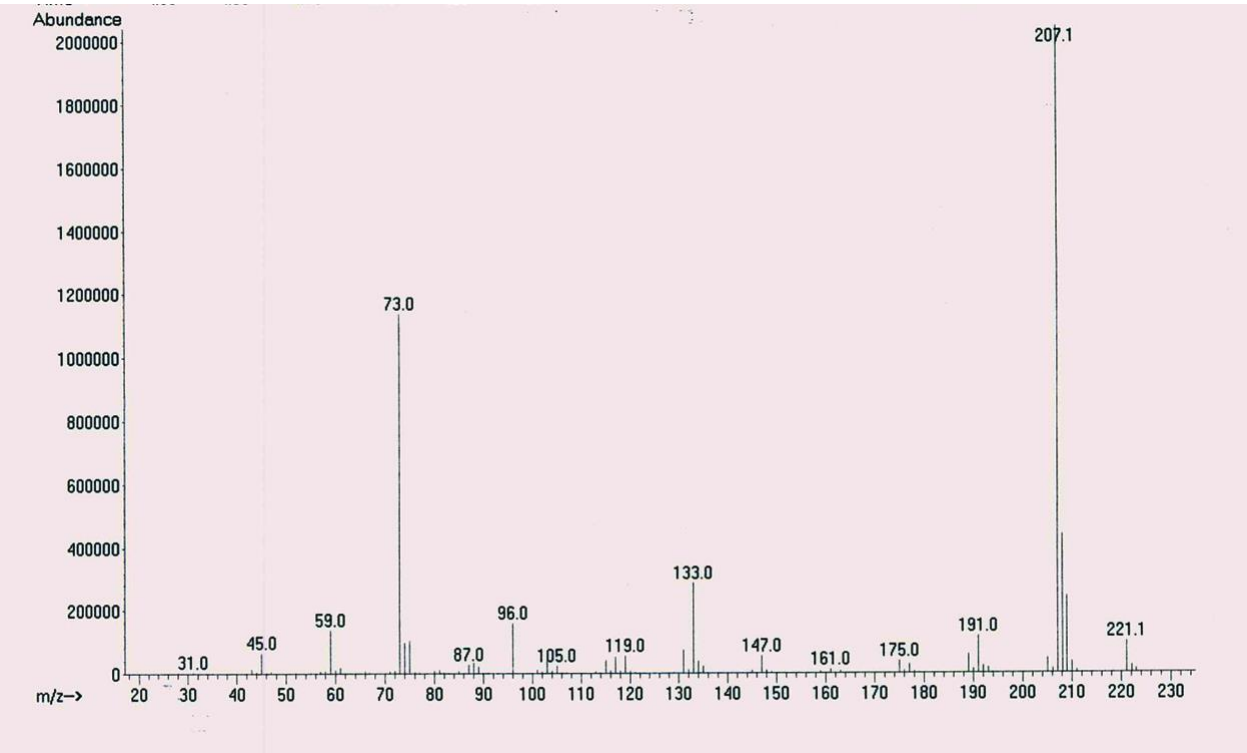


Figure 12: MS Pattern corresponding to HMTS.

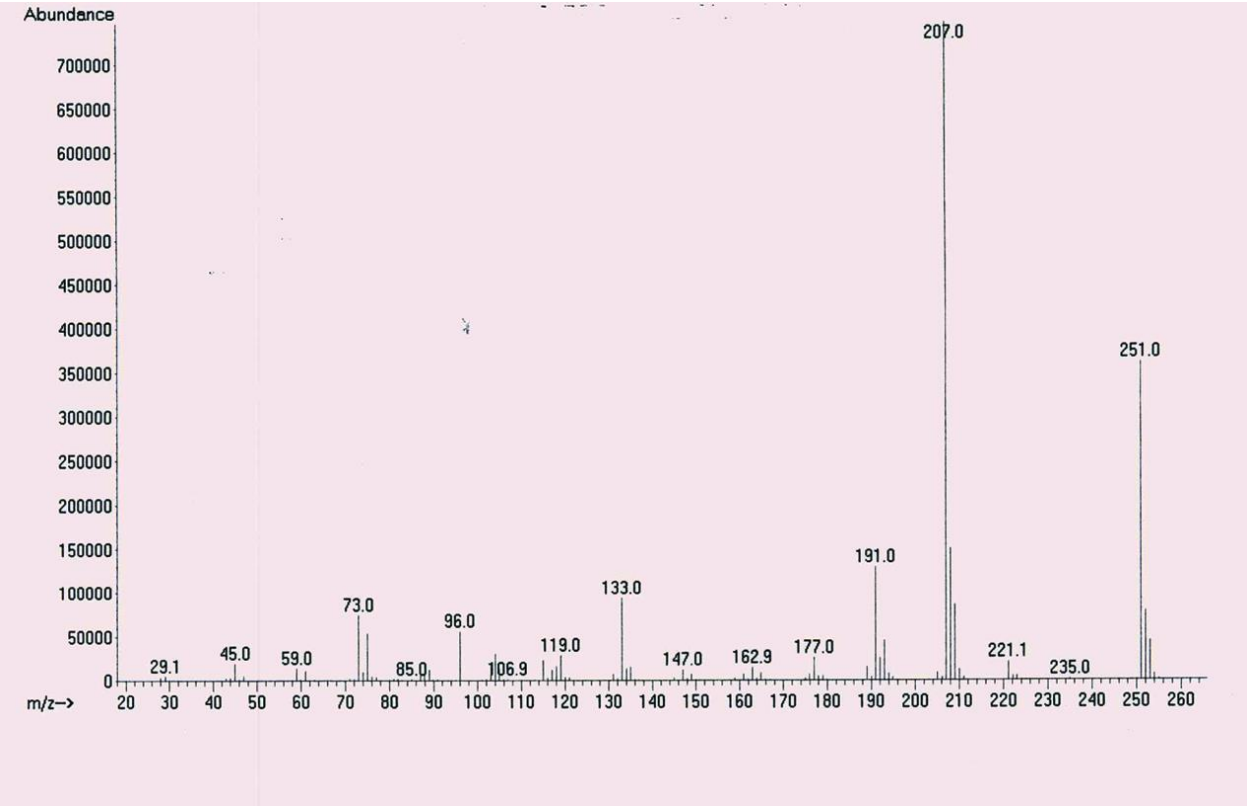


Figure 13: MS Pattern of the silyl formate.

3.3.2 CALCULATION OF MOLAR CONSTITUENTS OF REACTION

Based on the result from the GC-MS, the amounts in mole of the constituents of the reaction mixture were calculated as described below:

CALCULATION FOR HMTS

$$n_{si} = \frac{p_{si}}{100}\frac{m_0}{MM_{si}}$$

where n_{si}, p_i, m_0 *and* MM_{si} *are the number of mole of HMTS, percentage report by GC – MS, initial amount of HMTS feed and molar mass of HMTS respectively.*

CALCULATION FOR SILYL FORMATE

$$n_{sf} = \frac{p_{sf}}{100}\frac{m_0}{MM_{sf}} \qquad (1)$$

where n_{sf}, p_{sf}, m_0 *and* MM_{sf} *are the number of mole of HMTS, percentage report by GC* $-$ *MS, initial amount of HMTS feed and molar mass of Silyl formate respectively.*

Equation (1) make the assumption that the density of the reaction mixture does not change significantly with time. This assumption is reasonable since we don't have a significant increase (percentage increase is low because the starting material already has a high molecular weight of 222.5 and silyl formate has a molar mass of 266.5) in the molar mass of the major product which is silyl formate.

For the calculation of the time base concentration of siloxane in the reactor, the volume of the initial amount of HMTS charged (3ml) was used throughout the reaction. This is based on the above assumption.

CONVERSION CALCULATION

The fractional conversion, X, is defined as the amount in mole of the reactant (HMTS) that has been converted into product. It is given by the following relationship:

$$X = 1 - \frac{N_{si}}{N_{si0}}$$

where X is the fractional conversion, N_{si} *is the time based number of mole of HMTS and*

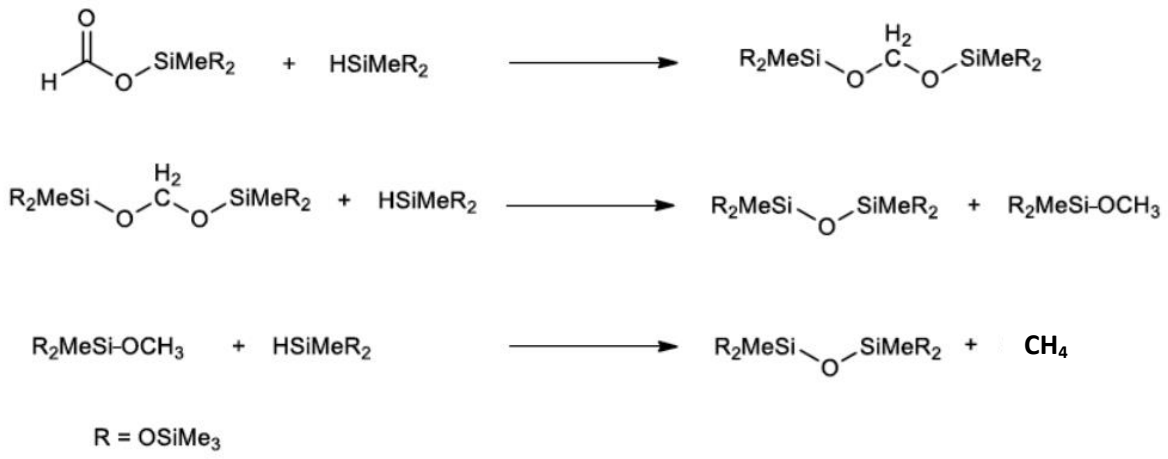
N_{si0} *is the number of mole of the initially charged HMTS*

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 RESULTS AND DISCUSSION FOR CATALYST 1

In this section, the results obtained for catalyst **1**, Ir(H)(CF_3SO_3)(NSiN)(coe), used in the experiment are reported and discussed. We have started the catalytic solvent-free hydrosilylation of CO_2 (25 ^oC, 3.0 bar) with HMTS to produce the corresponding silylformate using 1 mol% of the catalyst **1**. After 80 hr, the total consumption of HMTS to give yellow oil identified by ^1H NMR spectroscopy and GC-MS as a silylformate, (89% yield). GC-MS spectra of the reaction samples taken evidenced the full consumption of the starting HMTS and the presence of a peak with a retention time of 9.22 min corresponding to the silylformate (89% yield). The mass pattern found for that peak agrees with that expected for silylformate. An additional peak due to $\{(Me_3SiO)_2MeSi\}_2O$ appears at 19.79 min (9.4%). The presence of $\{(Me_3SiO)_2MeSi\}_2O$ could be due to further reactions of silylformate with HMTS under the reaction conditions (Scheme 3) or to some iridium-catalyzed hydrolysis of the starting hydrosilane.



Scheme 3: Possible transformations of in situ generated silylformate during CO_2 hydrosilylation processes.

KINETIC STUDY OF THE CATALYTIC HYDROSILYLATION OF CO_2 WITH HMTS AT DIFFERENT TEMPERATURES

Kinetic studies of the reaction of hydrosilylation of CO_2 with HMTS in the presence of 1 mol% Catalyst **1** show that the rate of this process is temperature dependent. The results from the kinetic studies of the reaction are depicted in Table 1 and figure 14. These results show the increase in the catalytic activity by increasing the temperature of the reaction from 25 °C to 75 °C. At 75 ^{o}C a higher catalytic activity was observed. GC-MS studies of the reaction evidenced that after 3 hours at that temperature most of the starting HMTS has been consumed and 87 % of silylformate is formed (figure 14 and Table 1). Temperatures above 75 ^{o}C were not studied because of the deactivation of the catalyst at temperatures above 80 ^{o}C. This result shows the

reduction of the reaction time required for the complete conversion of the HMTS from 80 hrs for the reaction at 25 ^{o}C to 3 hrs for 75 ^{o}C (figure 14).

Table 1: Raw data from the GC-MS for the hydrosilylation reaction at 3 bar and various temperatures

ROOM TEMPERATURE: 25 ^{o}C				
S/N	TIME (h)	HMTS (mol%)	SILYL FORMATE (mol%)	DIMER $(R_2MeSi)_2O$ (mol%)
1	12	99.4	0.6	0.0
2	24	97.7	1.5	0.8
3	36	88.2	9.9	1.9
4	48	56.9	37.8	5.3
5	60	23.2	70.4	6.4
6	72	6.8	83.8	9.4
7	80	1.8	88.8	9.4
TEMPERATURE: 35 ^{o}C				
8	8	98.9	0.8	0.3
9	17	89.2	9.1	1.8
10	24	55.8	40.0	4.2
11	32	11.8	82.4	5.8
12	41	1.4	91.1	7.5
TEMPERATURE: 45 ^{o}C				

13	3	99.5	0.5	0.0
14	7	95.4	3.4	1.2
15	11	56.9	39.3	3.8
16	14	22.3	71.5	6.2
17	23	0.9	91.1	8.0
TEMPERATURE: 55 ^{o}C				
18	2	96.8	2.1	1.0
19	4	50.3	44.8	4.9
20	6	13.5	79.5	6.9
21	8	3.2	89.7	7.1
22	9	1.5	87.2	11.3
TEMPERATURE: 65 ^{o}C				
23	1	71.4	25.8	2.9
24	2	32.2	60.7	7.2
25	3	17.7	78.0	4.3
26	4	9.2	85.8	5.1
27	5	4.9	85.8	9.3
TEMPERATURE: 75 ^{o}C				
28	0.5	58.7	39.9	1.4
29	1	27.5	69.4	3.1
30	1.5	17.8	79.3	2.9
31	2	10.4	83.1	6.5
32	2.5	4.6	90.2	5.2

33	3	2.3	87.1	10.5

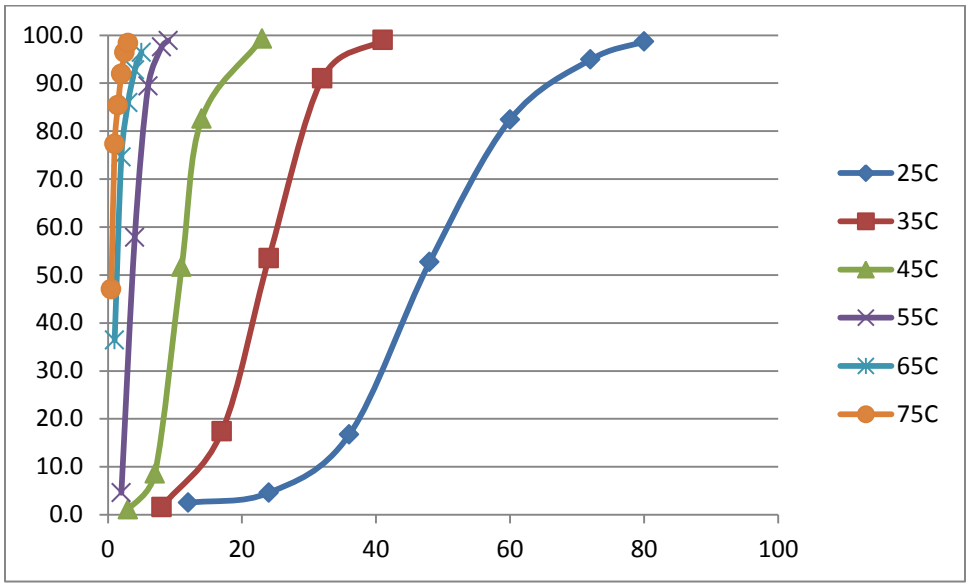


Figure 14: The experimental result for the hydrosilylation reaction at 3 bar and different temperatures

Based on the data from the GC-MS, TOF and the yield of silyl formate was calculated and the comparison between the values for a specific pressure and different reaction temperature. The definitions for the turn over frequency and the yield are given below:

$$TOF = \frac{mol\ of\ silylformate\ formed}{mol\ of\ catalyst\ used\ X\ time\ taken\ for\ reaction}$$

$$Yield = \frac{mol\ of\ silylformate\ formed}{mol\ of\ HMTS\ charged\ into\ the\ reactor}$$

Table 2: Turn over frequency and yield of formate for the hydrosilylation reaction at 3 bar pressure

Temperature (^{o}C)	Yield (%)	Turn over frequency (TOF) (/hr)
25	89	1.1
35	91	2.2
45	91	3.9
55	87	9.7
65	86	17.3
75	87	29.1

Table 3 shows the turn over frequency and the yield of the formate at different temperature and 3 bar pressure. Following the values obtained for the TOF, the catalytic activity of the Iridium catalyst was found to increase with the temperature as expected.

The results obtained from the GC-MS were translated into concentration of HMTS and this was used for the Kinetic modeling for the reactions. The number of mole of the HMTS remaining in the reactor at each time was calculated and the concentration determined with a volume V=3ml as shown below:

$$C_{si} = \frac{n_{si}}{V} \qquad (2)$$

$$where\ C_{si}\ is\ the\ concentration\ of\ HMTS, n_{si}\ is\ the\ number\ of\ mole\ of\ HMTS$$

$$and\ V\ is\ the\ intial\ volume\ of\ HMTS$$

4.2 EFFECT OF CO_2 PRESSURE ON THE HYDROSILYLATION REACTION

After kinetic studies on the reaction of CO2 with $HSiMe(OSiMe_3)_2$ in presence of a catalytic amount of catalyst **1** (1.0 mol%) at variable temperature and constant pressure (3 bar), the pressure screening study was performed to check the activity and selectivity of the reaction with the increase of pressure (1 bar to 8 bar). The screening of the reaction with different CO_2-pressures and temperatures shows that, the CO_2-pressure exerts an effect on the activity of the catalytic system (Table 3 and 4). After optimizing the temperature and CO_2 pressure, it is found that reaction condition of temperature 75 ^oC and 8 bar pressure gives high activity with turnover frequency ($TOF_{1/2}$) value of 138 h^{-1}.

The results show that CO_2-pressure has less influence at 25 ^oC on the catalytic activity (Table 4, entries 1, 4, 7, 10). At 55 ^OC, condition of CO_2-pressure of 1 and 3 bar has less influences on the activity (Table 4, entries 2 and 5). But when the pressure is increased from 3 bar to 6 bar, a visible increase in catalytic activity was observed ($TOF_{1/2}$ increased from 13.4 to 52 h^{-1} (Table 3 entries 5 and 8). At 8 bar pressure with the same temperature shows same activity as at 6 bar pressure (Table 3, entry 11). It is revealed that at temperature 75 ^oC with different pressures (1 bar to 8 bar), a clear positive effect on the activity of the catalytic system was observed. $TOF_{1/2}$ values were increased from 26 h^{-1} at 1 bar to 138 h^{-1}1 at 8 bar (Table 3 entries 3 and 12). Therefore, temperature has proven to be a determinant factor on the catalytic activity of this catalyst.

Table 3: Turn over frequency and yield of the hydrosilylation reaction at 1, 3, 6 and 8 bar pressure

S/N	**Temperature** (°C)	**CO_2-Pressure** (bar)	**Yield**	**$TOF_{1/2}$** (h^{-1})
1	25	1.0	0.81	1.2
2	55	1.0	0.79	9.0
3	75	1.0	0.81	26.0
4	25	3.0	0.89	1.2
5	55	3.0	0.87	13.4
6	75	3.0	0.87	92.0
7	25	6.0	0.88	1.3
8	55	6.0	0.83	52.0
9	75	6.0	0.91	116.0
10	25	8.0	0.71	1.6
11	55	8.0	0.84	53.0
12	**75**	**8.0**	**0.83**	**138.0**

Moreover, figure 15 represents the plot of conversion with time at 75 ^{o}C. The conversion of HMTS took the longest time (about 6 hours) for 1 bar to achieve 100% conversion, whereas, it took 3 hours for a CO_2 pressure of 3 bar.

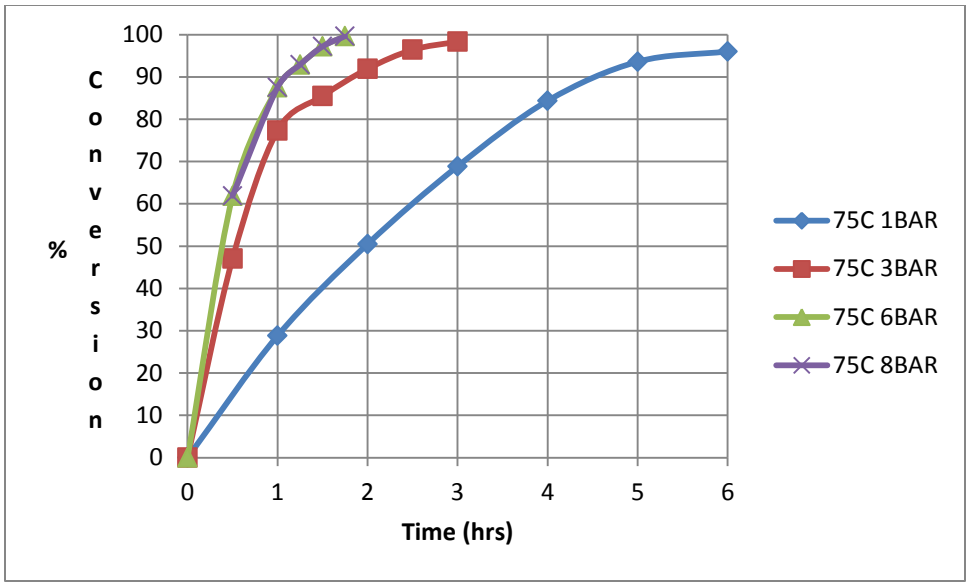


Figure 15: Effect of pressure on the conversion at 75 ^{o}C

The graph for 6 bar and 8 bar appears to be superimposed due to the time scale used. Figure 16 gives a clearer picture of the reaction conversion with time for the two pressures. Although the reaction rates at the initial stage of the reaction are almost the same, the reaction at 8 bar pressure became faster as the reaction progressed to completion at 105 minutes while that of 6 bar did not complete until 120 minutes. Similar results are also obtained for the remaining pressures and are shown in Figures 17.

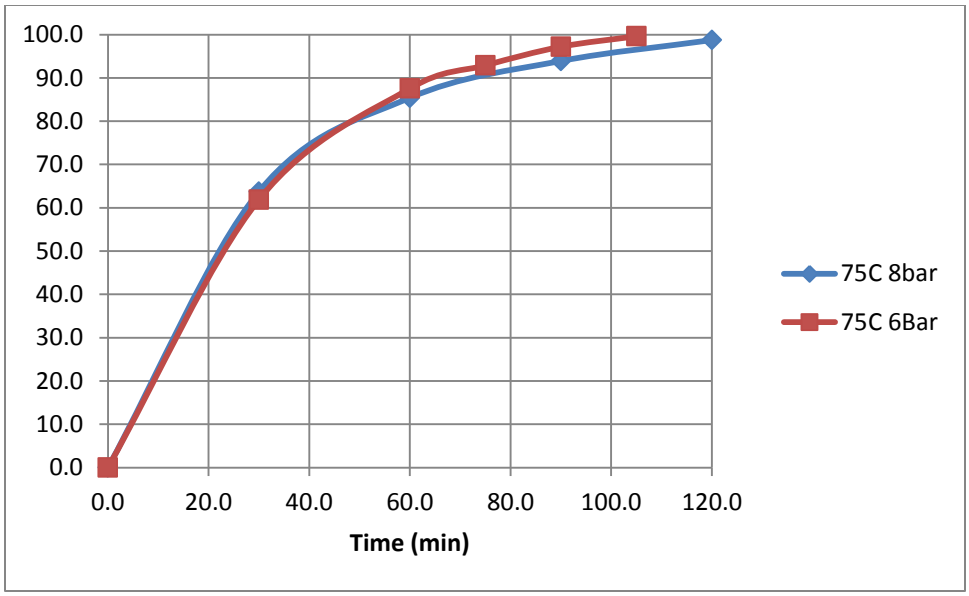


Figure 16: The pressure effect at 75 ^{o}C for 6 and 8 bar pressures

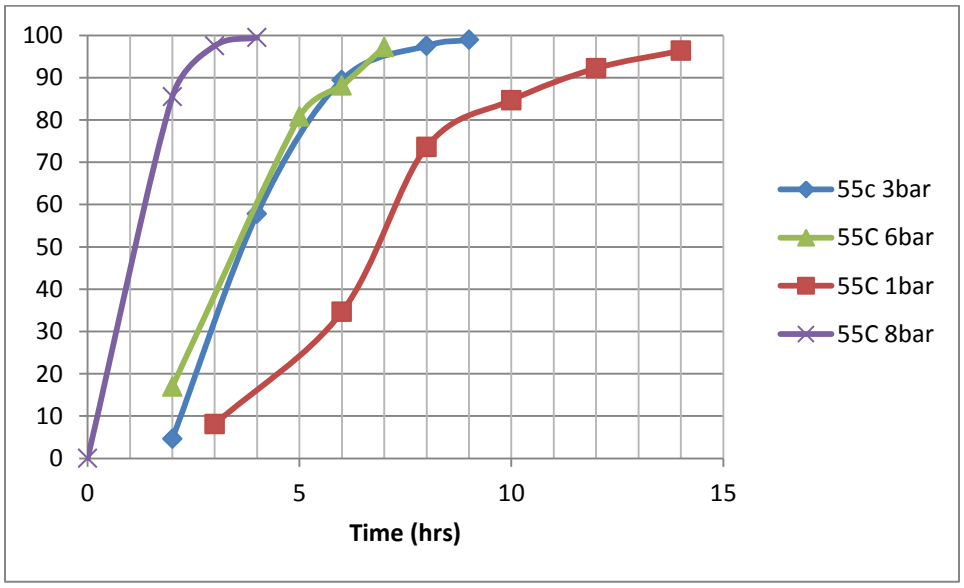


Figure 17: The effect of pressure at 55 ^{o}C

Most of the catalytic CO_2 hydrosilylation processes have lack of selectivity. This is due to the reaction of excess of hydrosilane with silyl formate in the presence of an hydrosilylation

catalyst, to afford the corresponding bissilylacetal, which then could react with silane to give the corresponding methoxysilane and siloxane (Scheme 3). Again, the reaction of methoxysilane with hydrosilane could afford the siloxane and methane [4]. Thus, not only the activity has to be determined but also the selectivity of catalyst is important in order to establish the reaction performance. It should be mentioned that at temperature 75 ^{o}C, each CO_2-pressure has the highest activities (Table 4). The selectivity to Silyl Formate is in the range of 80–90% (Table 4).

Table 4: Conversion of $HSiMe(OSiMe_3)_2$ and yield of the silyl formate obtained by the hydrosilylation reaction using catalyst **1** at 75 ^{o}C and variable CO_2 pressures

S/N	**CO_2-Pressure** (bar)	**Time** (hr)	**Yield** (%)	**Conversion** (%)
1	1.0	6.0	80.6	96.0
2	3.0	3.0	87.0	98.3
3	6.0	2.0	90.6	99.6
4	8.0	2.0	89.7	99.9

The highest selectivities and conversions were achieved with CO_2-pressure of 6 or 8 bar at temperature 75 ^{o}C (~90.0%) (Table 4). Hence, the best reaction conditions (best activity and selectivity) for this CO2 hydrosilylation process is with temperature 75 ^{o}C and CO_2 pressure 6–8 bar.

To ensure the quality of the experimental data, reproducibility studies were carried out previously to the kinetic modeling of the reactions (Figure 18).

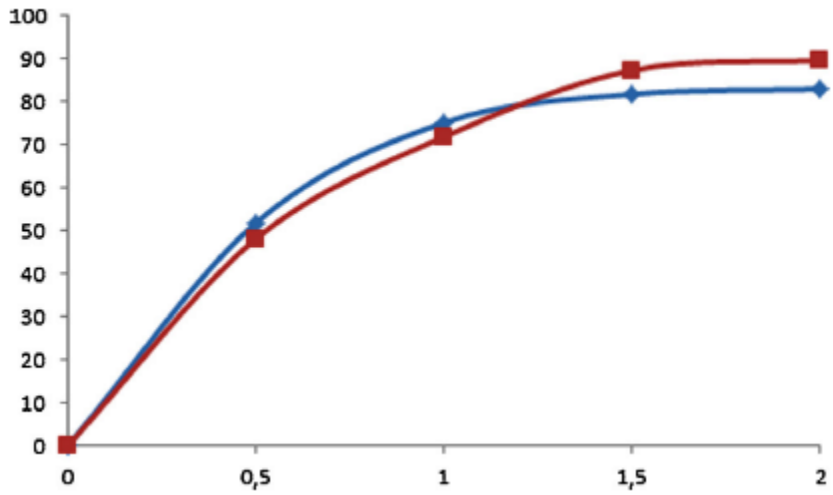


Figure 18: Reproducibility study for reaction at 75 ^{o}C and 8bar CO_2 pressure using catalyst **1**

The graphical presentation of conversion of HMTS and formation of silyl formate and $(R3Si)_2O$ are shown in figure 19.

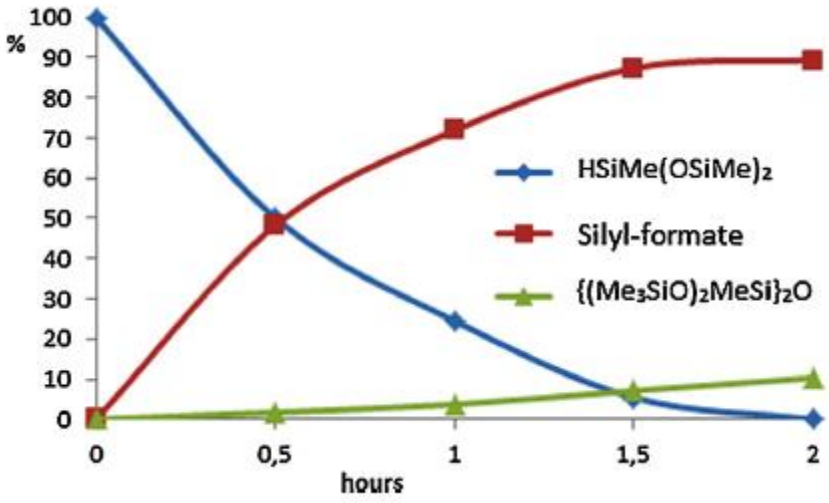


Figure 19: Time-dependence of the composition of the reaction samples at 75 ^{o}C and 8 bar pressure of CO_2 using catalyst **1**

GC–MS spectrum of the reaction product obtained and $(R_3Si)_2O$ are shown in Figure 20.

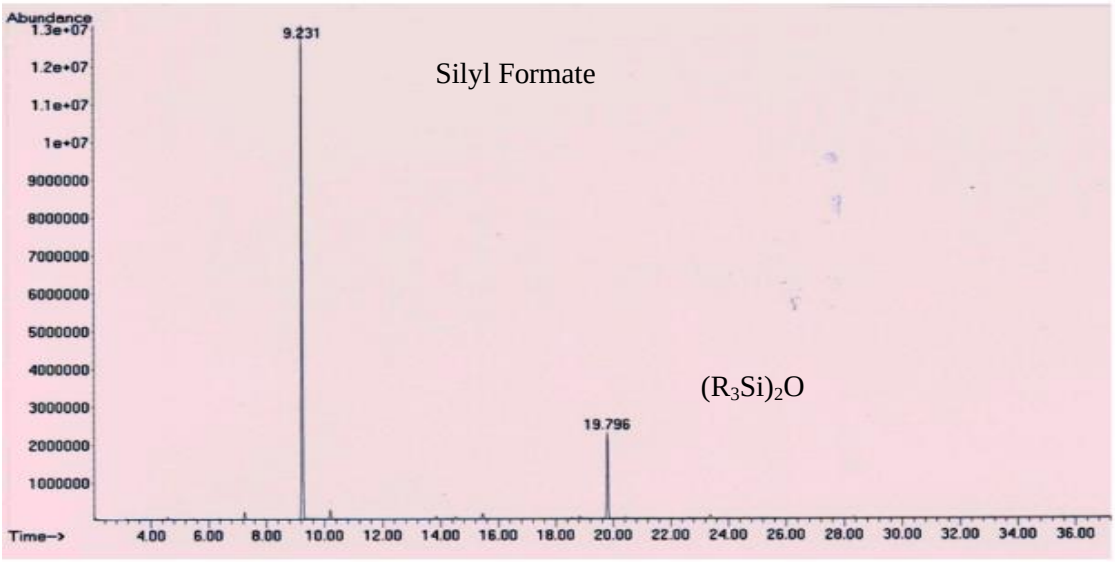


Figure 20: GC-MS spectrum of the reaction product obtained after 2 hr at 75 ^{o}C and 8 bar CO_2 pressure

4.3 CO_2 HYDROSILYLATION REACTION WITH CATALYST 2

Catalyst **2** [Ir(H)($CF3CO_2$)(NSiN)(coe)] is modified complex of catalyst **1**. The presence of a trifluoroacetate, instead of a triflate ligand in complex **2** produces an enhancement of the activity of the resulting catalytic system compared to that found for complex **1**. At 25 ^oC, the hydrosilylation reaction of CO_2 (3 bar) with HMTS in presence of catalytic amounts of complex **1** (1.0 mol%) requires 80 h to give the corresponding hydrosilylation product, silylformate in 89% purity. However, under the same reaction conditions complex **2** only needs 30 h to produce silylformate in 97% purity. It is worth noting that using **2** as catalyst precursor, a slight increase in the reactor temperature from 25 ^oC to 55 ^oC, produces an enhancement of the reaction performance. Thus, at 55 ^oC and using 8 bar of CO_2 it was possible to achieve the quantitative conversion of the HMTS to yield silylformate (96% purity) after 2.5 hours (Table 5, entry 2). When using lower CO_2 pressures 6 or 3 bar, it has required longer reaction times, 5 hr and 7 hr respectively, to reach the full conversion of the starting HMTS into silyl formate. The control of the temperature of the reactor has proven to be a relevant factor for tuning the activity and selectivity of the reaction. Indeed, working at 75 ^oC, regardless of the reactor CO_2 pressure (3 to 8 bar), and using **2** as catalyst precursor, a decrease in the selectivity of the CO_2 reduction process was observed. Hence, under the reaction conditions of 75 ^oC and 8 bar of pressure, the concentration of the side product, namely $O\{SiMe(OSiMe_3)_2\}_2$, grew to a value of 14.9% (Table 5, entry 4). We have found that in the range of temperatures from 25 ^oC to 55 ^oC, independently of the CO_2 pressure, complex **2** is more active and selective than **1**.

Table 5: Conversion and selectivity for the catalytic hydrosilylation of CO_2 (8 bar) with HMTS using complex (1 and 2) (1.0 mol%) as precatalyst. All the data are based on quantitative GC-MS analyses.

Entry	T (^oC)	Catalyst	Time (h)	Conversion[a]	Yield[b]
1	55	1	4	99.6	84.1b (15.3)[c]
2	55	2	2.5	99.4	96.1b (3.1)[c]
3	75	1	2	99.6	89.7b (10.3)[c]
4	75	2	1.5	99.2	84.0b (14.9)[c]

(a) [100 – wt% of HMTS]; (b) [(mmol of silylformate/initial mmol of HMTS) x 100]; (c) (in brackets mol% of $O\{SiMe(OSiMe_3)_2\}_2$).

4.4 KINETIC MODELLING

The experimental data obtained were used for the regression analysis for the kinetic parameter estimation. MATLAB software was utilized for this purpose. The following toolboxes and their purposes were used in the MATLAB code:

NLINFIT: This statistical toolbox was used for the nonlinear regression analysis for the estimation of the kinetic parameters. This toolbox makes use of Levenberg-Marquardt algorithm. It has an advantage over the 'NonLinearModel.fit' toolbox in that the optimized parameter estimated can be utilized within the code for plotting the experimental data and the modeling result on the same graph.

ODE45: This MATLAB function makes use of the 4^{th} order Runge-kutta numerical solution for to solve non-stiff differential equation. Since the mole balance equation to be solved is a first-order, non-stiff differential equation, the function is invoked to solve the resulting differential equation.

The flow chart for the kinetic modelling is as shown in figure 21. The experimental data directly from the GC-MS is imported into the MATLAB Workspace. Then the reaction conditions were described before invoking the NLINFIT toolbox with an initial guess for the kinetic parameters, both the activation energy, E and the rate constant k_0 at 50 ^{o}C. The NLINFIT optimizes the kinetic parameters until the kinetic parameter value that gives the best fit, lowest SSR, an r-square value close to unity, and a tight confidence interval is obtained. These obtained values for the kinetic parameters were then used to solve the mole balance differential equation and the experimental data plotted with the model. For all the conditions studied, the obtained graph fitted well with the experimental data.

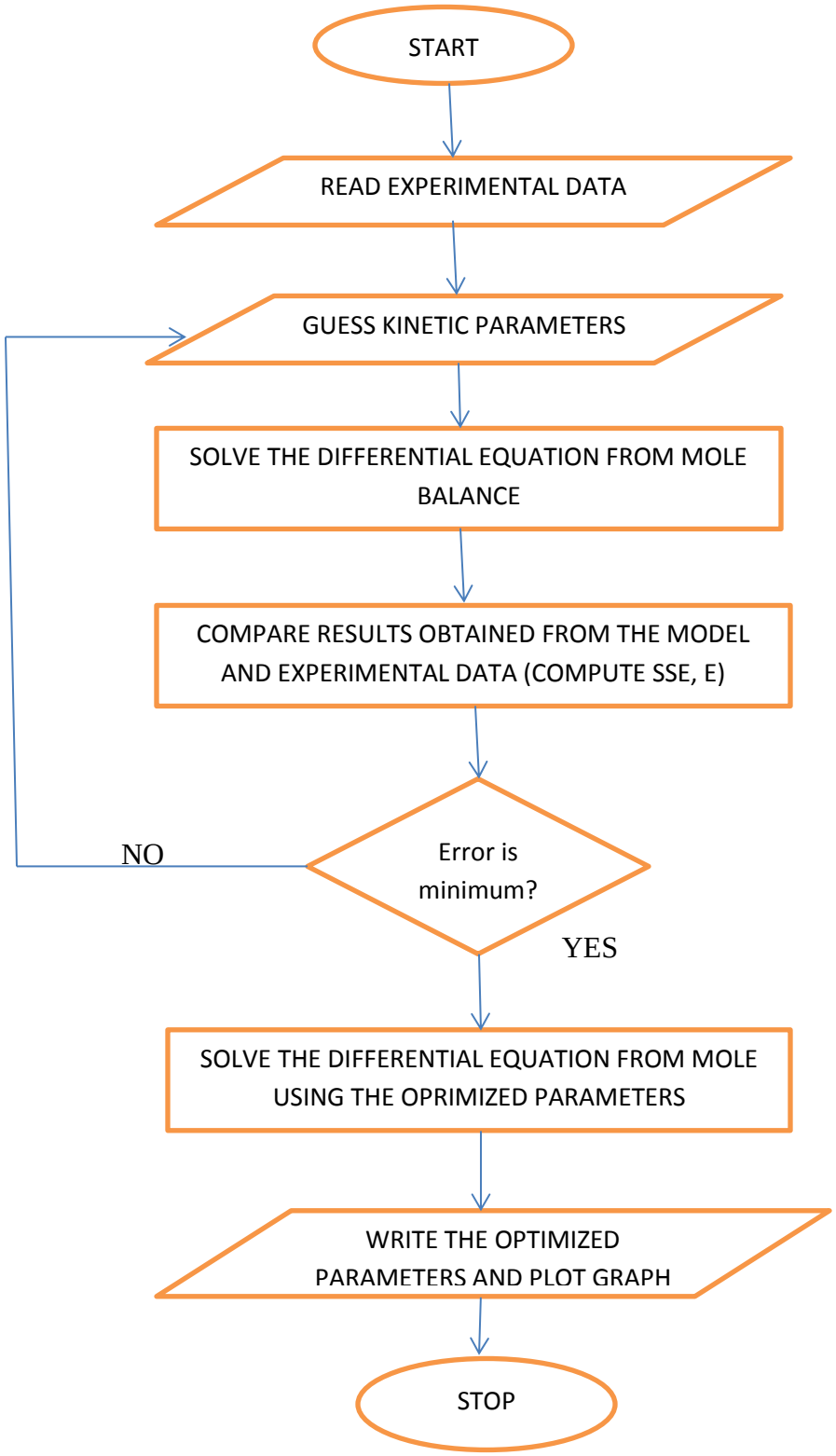


Figure 21: The flow chart for the kinetic parameters estimation

4.5 KINETIC MODELING OF THE CATALYTIC HYDROSILYLATION OF CO_2 WITH $HSiMe(OSiMe_3)_2$

It was assumed that the volume of the reaction mixture remains constant during the catalytic process, which is reasonable since the density does not change appreciably. A power law model was proposed for the homogeneous reaction. In addition, we have considered a first-order reaction with respect to $HSiMe(OSiMe_3)_2$. So, the rate of disappearance of $HSiMe(OSiMe_3)_2$ (Eq. 1) can be written as:

$$-V\frac{dC_{sx}}{dt} = V\frac{dC_f}{dt} = k_i C_{sx} W_c \qquad (3)$$

where, C_{sx} and C_f are the molar concentrations of $HSiMe(OSiMe_3)_2$ and SF in the reaction mixture, respectively, V is the initial volume of $HSiMe(OSiMe_3)_2$, W_c is the weight of the catalyst, t is the time in hours and k_i is the rate constant.

MATLAB ODE45 subroutine, which utilizes the 4^{th} order Runge-Kutta method, was used to solve the resulting equations and the parameters were estimated with the described non-linear regression (see ESI). The values of k_0 and E were estimated using a non-linear regression.

4.5.1 KINETIC MODELING OF THE $Ir(H)(CF_3SO_3)(NSiN)(coe)$ CATALYZED REACTION

This section entails the kinetic study and modeling of the solvent-free **1**-catalyzed hydrosilylation of CO_2 with $HSiMe(OSiMe_3)_2$ at various pressures of CO_2 (3, 6 and 8 bars). The

effect of the CO_2-pressure on the above mentioned catalytic process was modeled using the power law model considering a first-order reaction with respect to $HSiMe(OSiMe_3)_2$. As mentioned earlier, the Figure 6 represents the structure of the catalyst.

CO_2 was in excess during the course of the reactions and therefore its concentration is assumed to be constant throughout the catalytic processes. A mole balance carried out on the reactant, $HSiMe(OSiMe_3)_2$, and the product, SF, yielded coupled differential equations.

The kinetic study shows a clear temperature dependence of the reaction rate. Figures 22 and 23 display the experimental data obtained from the GC-MS, as circles, and the model prediction, as continuous lines, for CO_2-pressures of 6 and 8 bar. An increasing of the temperature from 55ºC to 75ºC produces a positive effect on the reaction rate as it was expected. Furthermore, at 55ºC an enhancement of the CO_2-pressure from 6 to 8 bar significantly reduces the time of reaction completion from 7 to 4 hours, which implies that the catalytic activity is increased. However, at 75ºC, an increase of the CO_2-pressure from 6 to 8 bar produces no significant effect on the reaction rate, with both reactions finishing within 2 hours.

During the optimization process, the parameters evaluated, pre-exponential factor and activation energy, were ensured to have physical meanings. Only positive parameter values were determined, the sum of square error was minimal and a tight confidence interval for each parameter was ensured. Other criteria used in the estimation are minimal cross-correlations coefficient (γ) and the coefficient of determination (R^2) was almost unity. With 95% confidence interval, the estimated kinetic parameters and graphs (both experimental and fitted curves) were obtained following the described procedure.

From the Table 6, it can be concluded that there is no significant change in the activation energy with changing the CO_2-pressure. Furthermore, it was observed that the activation energy is around 72 kJ mol^{-1} for the CO_2 pressures of 3, 6 and 8 bar. Which suggest that under the explored reaction conditions the activation energy is CO_2-pressure independent. This is in agreement with previous studies reported by Roberts and Harris [29].

Table 6: Activation energy and pre-exponential factor values for the catalytic hydrosilylation using catalyst **1** at different CO_2-pressures.

Entry	**CO_2-Pressure** (bar)	**Activation energy (E)** (kJ mol^{-1})	**Pre-exponential factor (k_0)** (h^{-1} $gcat^{-1}$)
1	3.0	73.8±2.9	31.05
2	6.0	74.4±2.3	47.05
3	8.0	68.1±3.3	42.60
Average		72.1	

Following the Arrhenius equation, the pre-exponential factor and activation energy in the above table were used to solve the coupled differential equations. The results from this mathematic treatment, for the reactions carried out at 6 and 8 bar of CO_2, are depicted in figures 22 and 23 as continuous lines. In addition, these figures show the experimental data obtained from the GC-MS studies of the reaction samples as circles. The results from the kinetic model show a clear

dependence of the conversion with the temperature for each CO_2-pressure and confirm that the CO_2-pressure plays a minor role. Moreover, these curves obtained using the activation energy and pre-exponential factor predicted fits well with the experimental data.

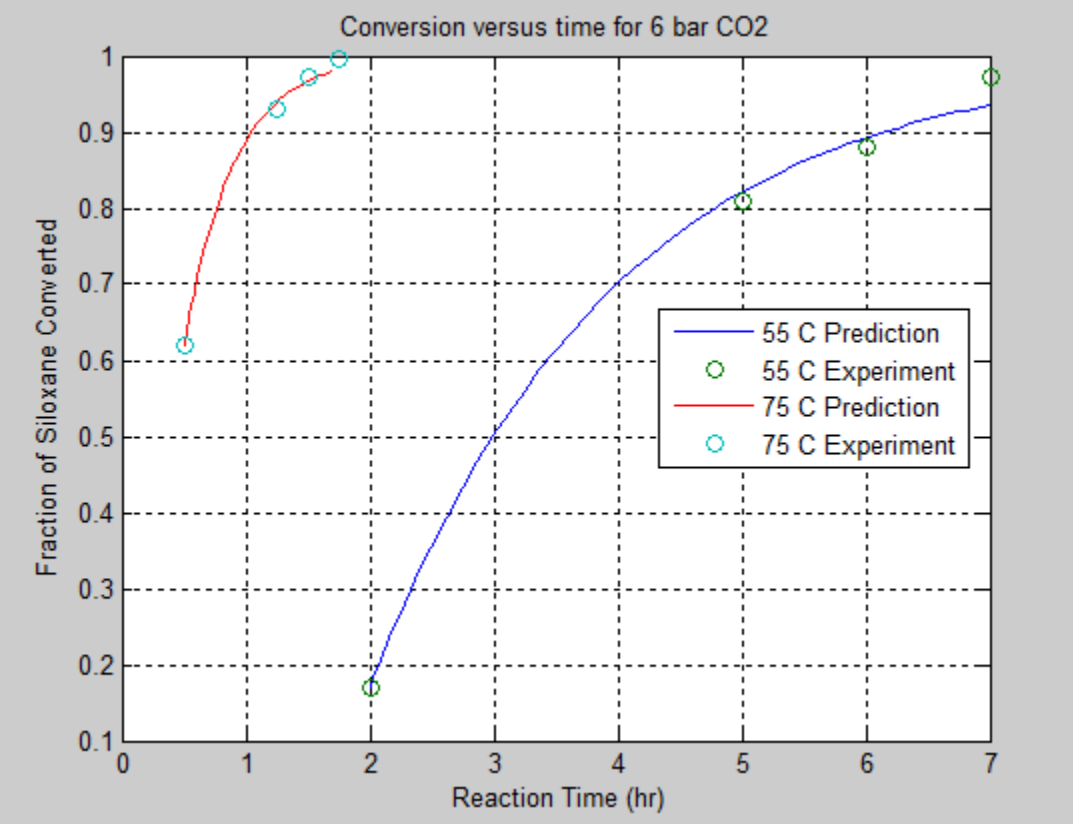


Figure 22: Comparison of the kinetic model with experimental data at 6 bar CO_2 pressure with catalyst **1**

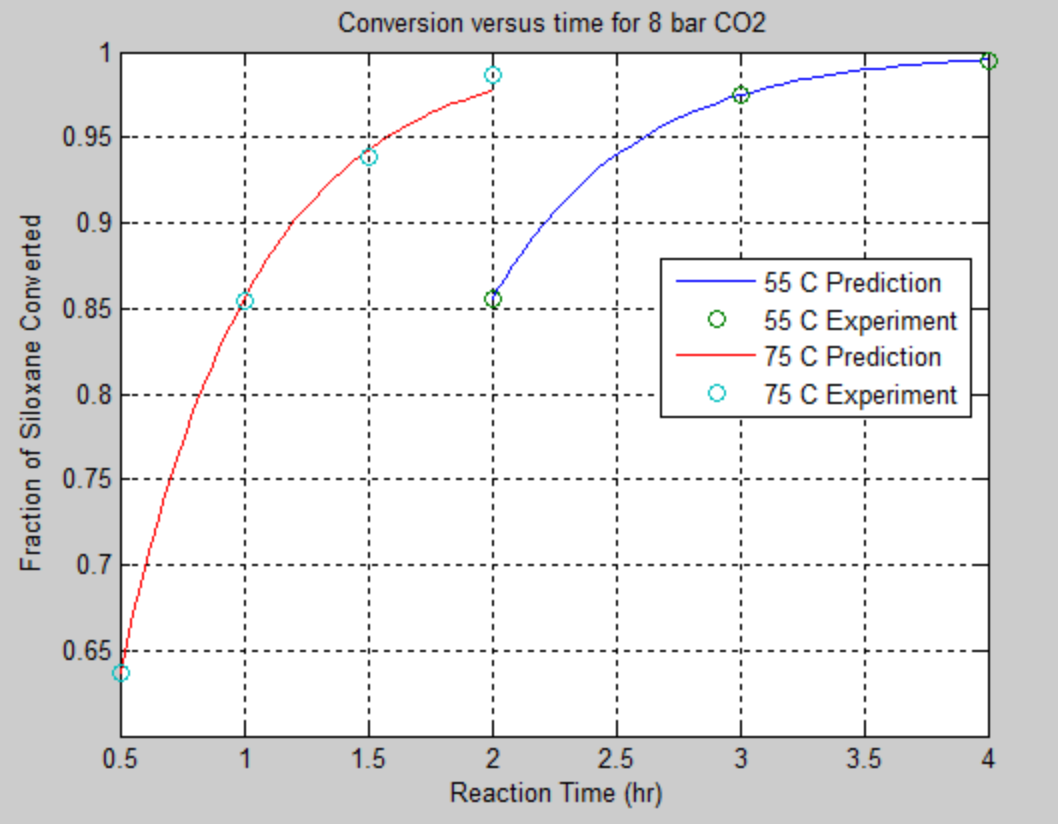


Figure 23: Comparison of the kinetic model with experimental data at 8 bar CO_2 pressure with catalyst **1**

4.5.2 KINETIC MODELING FOR THE Ir(H)(CF_3OCO)(NSiN)(coe) CATALYZED REACTION.

The modification of the catalyst synthesis step led to the second catalyst used for the same reaction and the kinetics of the reaction also studied. The chemical structure of the catalyst is as shown in Figure 7.

4.5.2.1 DETERMINATION OF THE ORDER OF THE REACTION

Based on the trend of the experimental data as shown in figure 24, a zero-order reaction is suggested and therefore, the kinetic model for the reaction is as follows:

$$-\frac{V}{W_c}\frac{dC_{sx}}{dt} = k$$

$$where\ V\ is\ the\ volume\ of\ siloxane\ feed\ used$$

$$C_{sx}\ is\ the\ time-dependent\ concentration\ of\ siloxane$$

$$t\ is\ the\ time\ in\ hours$$

$$k\ is\ the\ rate\ constant$$

$$W_c\ is\ the\ weight\ of\ the\ catalyst\ in\ gram$$

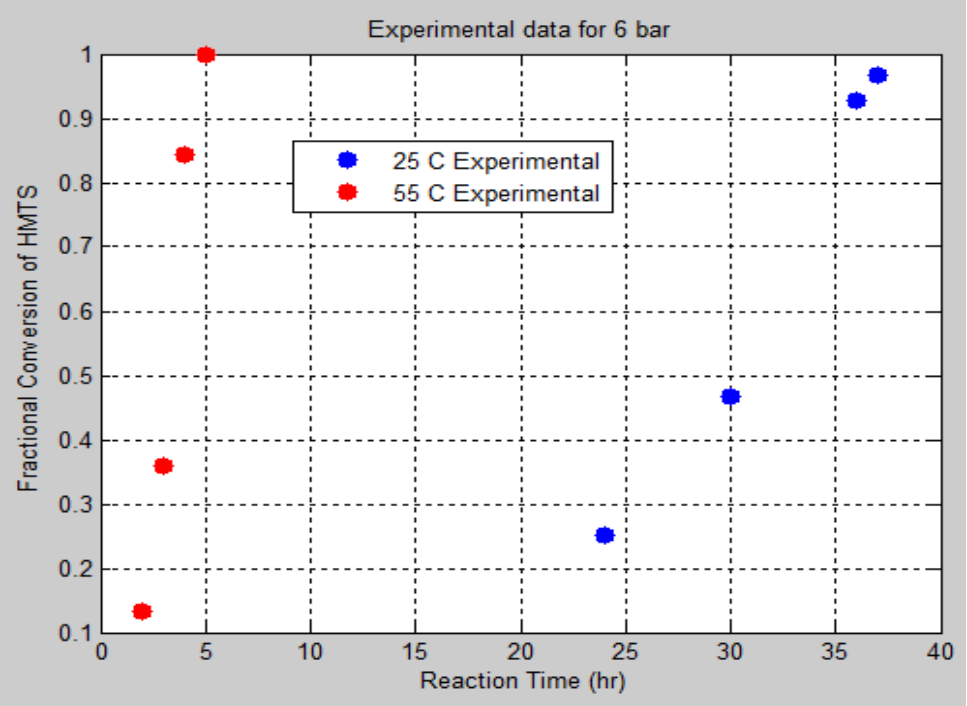


Figure 24: Plot of the conversion of HMTS against time for carbon dioxide at a pressure of 6 bar

The suggestion of zero as the order of the reaction is justified below:

A critical look into the graph reveals that the experimental data does not follow an exponential equation due to the fact that the points can easily be joined by a straight line. At 55 ^{o}C, it is further clear that even at 100% conversion, the straight line still predicts the experimental data perfectly. Similarly, at 25 ^{o}C, a straight line can be used for the prediction of the conversion up to the 97% conversion where the reaction was stopped. Thus, it is concluded that the order of the reaction is zero. As a further confirmation of our model, the experimental data for the CO_2 pressure 3 and 8 bar gave a very similar trend of a linear graph prediction of the experimental data.

A simple integration of the modelling equation yields:

$$C_{sx} = C_{sx0} - \frac{kW_c}{V}t \qquad (4)$$

$$where\ C_{sx0}\ is\ the\ initial\ concentration\ of\ siloxane$$

The above equation is used for the prediction of the experimental data with all the parameters in the equation constants except the time, t and the concentration, C_{sx}. This equation is the equation of a straight line of the form, $y = mx + c$.

4.5.2.2 ESTIMATION OF THE KINETIC PARAMETERS

For the calculation of the kinetic parameters, MATLAB was used for the computation of the kinetic parameters following the described non-linear regression. The values of k_0 and E were estimated using a non-linear regression. Only positive parameter values were determined. The sum of square error was minimal and a tight confidence interval for each parameter was ensured. Minimal correlations (γ) and the coefficient of determination (R^2) was almost unity. Figures 25, 26 and 27 shows the plot of the experimental data and the prediction super-imposed.

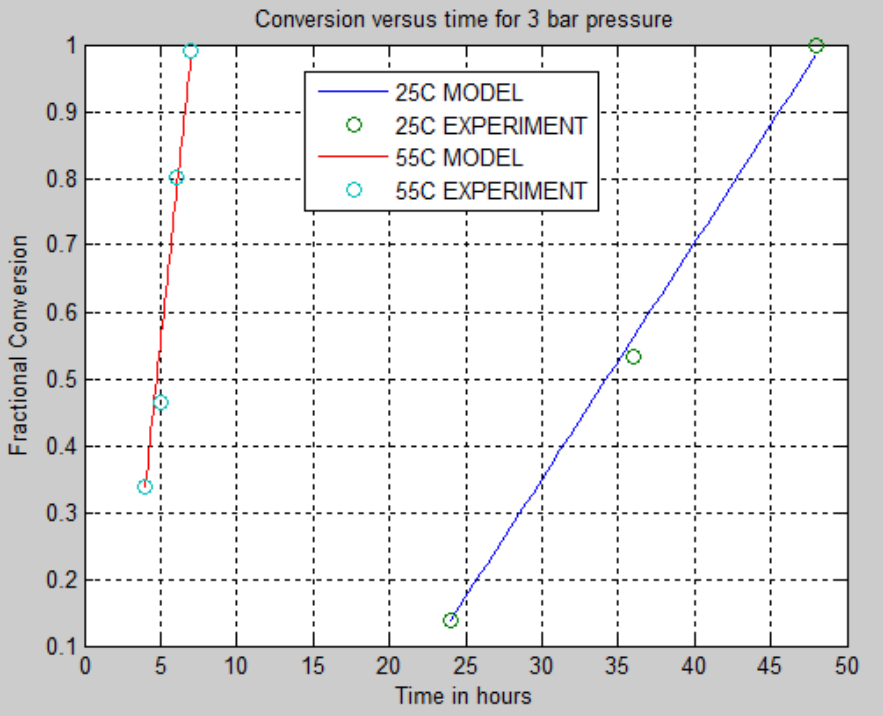


Figure 25: Comparison of the kinetic model with experimental data at 3 bar pressure with catalyst **2**

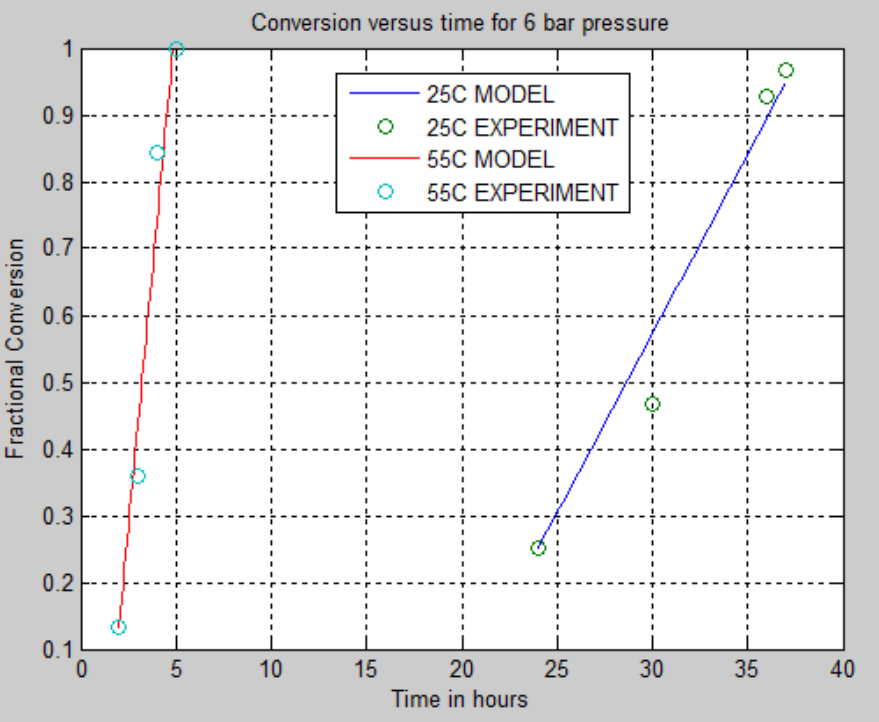


Figure 26: Comparison of the kinetic model with experimental data at 6 bar pressure with catalyst **2**

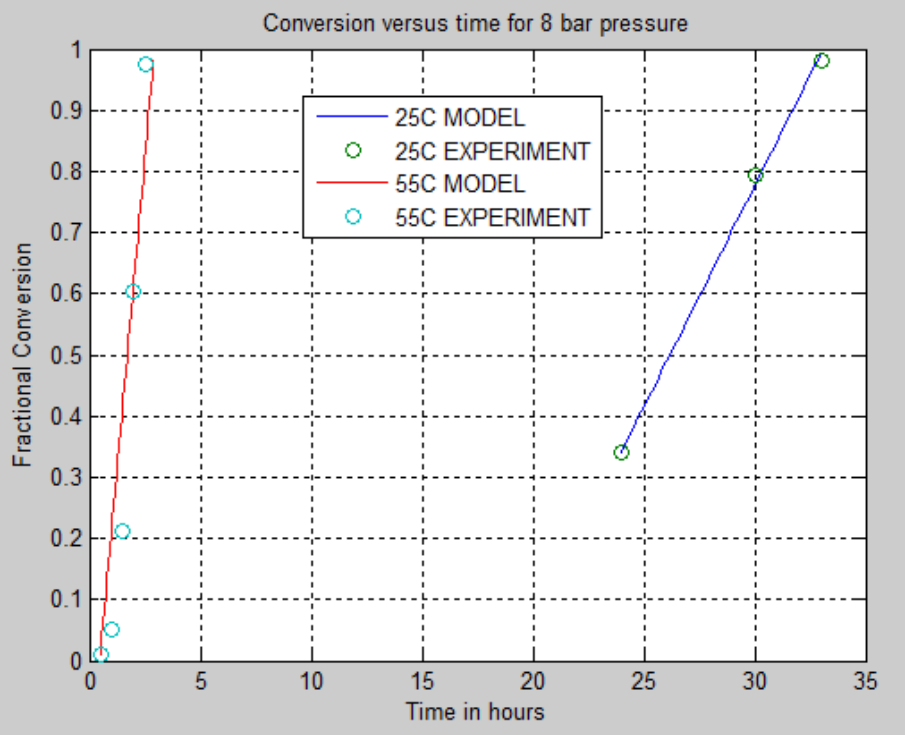


Figure 27: Comparison of the experimental data with the kinetic model at 8 bar pressure for catalyst **2**

Table 7: Activation energy and pre-exponential factor values for the catalytic hydrosilylation using catalyst **2** at different CO_2-pressures.

Entry	**CO_2-Pressure** (bar)	**Activation energy (E)** (kJ mol^{-1})	**Pre-exponential factor (k_0)** ($mol/cm^3/hr/gcat$)
1	3.0	48.9	0.0246
2	6.0	46.99	0.0352
3	8.0	46.68	0.047

Average	47.5

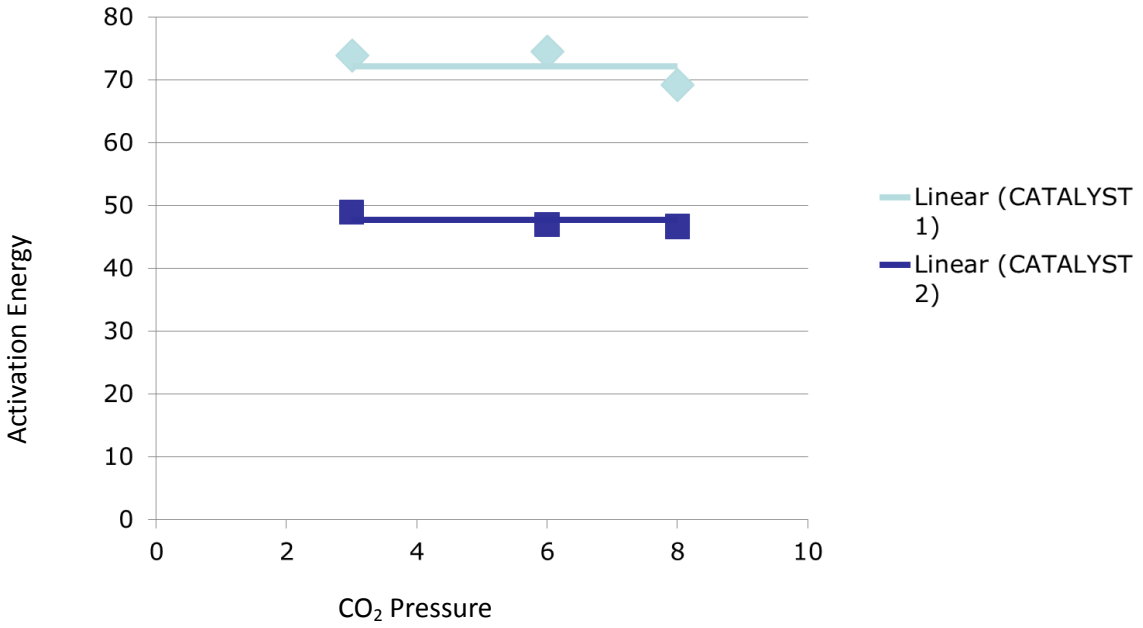


Figure 28: Effect of CO_2 pressure and catalyst type on the Activation Energy

4.6 DISCUSSION OF RESULTS

Table 6 shows that pre-exponential factor increases as the pressure of the CO_2 is increased. Although no research has been done on the solubility of CO_2 in HMTS, an explanation based on the modelling result obtained is the increase in the solubility of CO_2 as the pressure increases. When the solubility increases, it is expected that the concentration of the gas in the HMTS also increases. This has brought about the increase in the k value. An explanation for this is that the

rate of reaction is dependent on the concentration of CO_2. And since the consumed carbon dioxide during the reaction is replenished by the high pressure gas, the concentration remained constant throughout each operating condition

Based on the orders of the reactions, the reaction catalyzed by Ir(H)(CF_3SO_3)(NSiN)(coe), is best operated in a flow reactor while for the Ir(H)(CF_3OCO)(NSiN)(coe) catalyzed reaction either a batch or flow reactor can be utilized. As it is expected, the rate of the reaction for the catalyst **1** decreases as the reaction proceeds due to its reaction order. Therefore, the flow reactor to be utilized, for the case of 6 bar 55^oC, must have a conversion around 80% in order to have a reasonably sized reactor. This is because beyond this conversion of 80%, the catalyst **2** gives a better rate of reaction and may be preferred over catalyst **1**. The use of this flow reactor for the specified conversion will necessitate a separation unit to separate the silylformate product from the unreacted HMTS. Although the boiling point of the silyl formate was not studied in this research, future work on this area will require its determination. The separation process will therefore incur an additional cost for the process. If the conversion for the reactor designed exceeds 80%, the rate of the reaction with catalyst **1** will be lower than that of catalyst **2**, subsequently, a larger reactor volume will be required. In addition, a separation unit will also be required, thereby making the cost of equipment and processing exorbitantly high.

One of the possible reasons for the change in the order of the reaction when catalyst **2** was used is the change in the mechanism of the reaction. For catalyst **1**, the attack was launched by the HMTS and then the carbon dioxide reacted with this intermediate. However, in the case of catalyst **2**, the attack was launched by the carbon dioxide and followed by the reaction of the HMTS with the intermediate.

The variation of the carbon dioxide pressure from 3 up to 8 bar did not have any significant effect on the activation energy. The activation energy was maintained around 72 kJ/mol for the catalyst **1** with the pressure variation. Similar effect was observed in catalyst **2** with the activation energy staying at around 48 kJ/mol with this catalyst. Figure 28 shows the effect of varying the pressure and changing the ligand in the catalyst on the activation energy. It is further observed that there was a reduction in the activation energy when the catalyst **2** was used from 72 kJ/mol to 48 kJ/mol.

4.6.1 DESIGN OF A CSTR

The design equation for the CSTR derived from the mole balance is as follows:

$$V = \frac{X_{si} F_{si0}}{-r_{si}} \qquad (5)$$

Where X_{si} is the conversion of HMTS, $F_{si0}$is the molar flow rate of siloxane into the reactor, $-r_{si}$ is the rate of consumption of HMTS and V is the volume of the reactor.

For the catalyst **1**, the rate $-r_{si}$, is dependent on the concentration of the HMTS reactant and since the reactant concentration will be reducing as the reaction progresses, the rate also reduces. However, in the case of catalyst **2**, the rate remains constant no matter how much reactant is left in the reactor.

Following the above analysis, equation 5 implies that achieving 100% conversion for catalyst **1** will require a reactor of infinite volume since the rate will approach zero at this conversion while 100% conversion can be achieved with the catalyst **2** requires a reactor of volume

$$V = \frac{F_{si0}}{k}$$

If two reactors of same volume are used for both catalysts, with 100% conversion for the second catalyst, the conversion for the first catalyst will be given by:

$$X = \frac{k_1 C_{si0}}{k_1 + k_2 C_{si0}}$$

The derived equation above for the conversion of catalyst **1** using reactors of the same volume for catalysts **1** and **2** implies that it will be very difficult to achieve 100% conversion with this condition. This gives rise to separation of the HMTS remaining in the reactor effluent.

If we use two flow reactors of the same volume for both catalysts **1** and **2**, Figure 29 shows the equivalent conversion for the two conditions. It is clear from the graph that at 80% conversion using catalyst **1**, the corresponding conversion for catalyst **2** is also 80%. However, in a system whereby 83% conversion is achieved with catalyst **1**, replicating the same condition for catalyst **2** will yield 100% conversion for this system. In general, in order to have a conversion greater than 80% for catalyst **1**, the reactor volume required will be larger than that required for catalyst **2** with the same conversion.

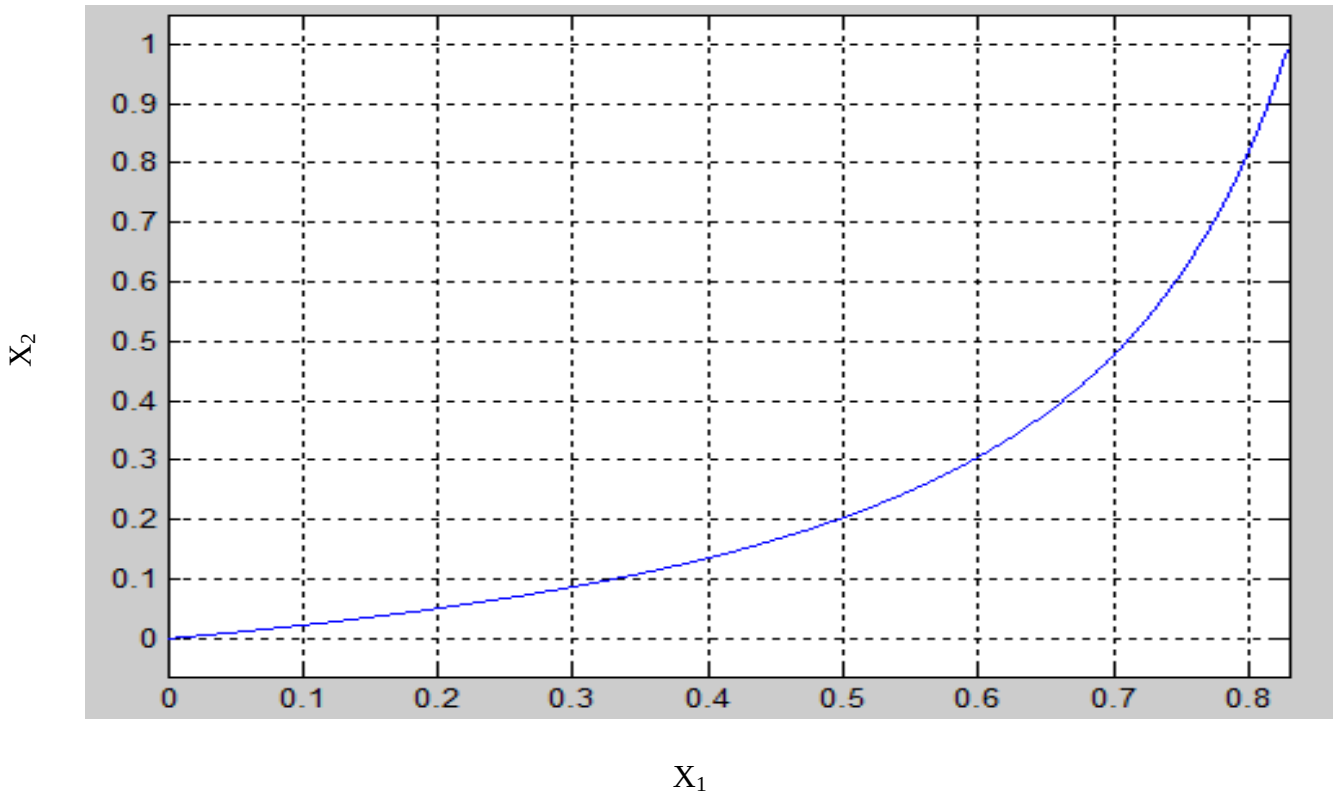


Figure 29: Plot of conversion of catalyst **1** against catalyst **2** using flow reactor of same volume

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The catalytic activity of various Ir-NSiN-type catalysts precursors containing different ancillary ligands in CO_2-hydrosilylation processes has been studied. The results from these experiments evidenced that the activity and selectivity of these Ir catalysts depend on the nature of the ligands as well as on the reaction parameters (temperature and CO_2 pressure). The best catalytic performance has been achieved at 55 ^{o}C and 8 bar of CO_2 using complex **2** (1.0 mol%) as catalysts precursor. Under reaction conditions the above mentioned catalytic system allows the solvent-free conversion of HMTS to the corresponding silyl formate (96.1% of purity) in 2.5 hour. Thus, by changing the different parameters like temperature, pressure and catalyst modification has allowed a reduction of the reaction time from 80 hours to 2.5 hour.

Temperature Effect: Temperature has a positive effect on the hydrosilylation reaction-Reaction time has reduced from 80hr to 2.5 hr. The rate constant is dependent on the temperature and predicted with the Arrhenius equation.

Pressure Effect: The pressure effect on the activity of the reaction is less compare with the temperature effect. The activation energy was independent of the pressure.

Catalyst 1 vs Catalyst 2: The Catalyst **2** shows more active and selective compared to Catalyst **1**. The activation energy is reduced from an average of 72 kJ/mol (for Catalyst **1**) to 47.5 kJ/mol for Catalyst **2**.

Kinetic Model: Power law model was used for the rate law to predict the experimental data

5.2 RECOMMENDATIONS

1. Due to the deactivation of the catalyst at temperatures above 80 ^{o}C, the reaction could not be studied above this temperature. An entirely new catalyst that will be able to withstand temperatures above 80 ^{o}C should be synthesized. Since the rate of the reaction for the hydrosilylation reaction increases with temperature, this will lead to an increase in the reaction rate and therefore a time for the completion of the reaction.

2. The catalyst used in this reaction is air-sensitive, a synthesis of a catalyst that is not air-sensitive will give more confidence in the industrialization of this process.

3. A flow reactor such as the CSTR should be used for the hydrosilylation reaction with both catalysts 1 and 2. The effect of the catalyst on the required reactor volume required for a preset conversion should be studied and comparisons made.

REFERENCES

[1] H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland, and I. Wright, "Progress in carbon dioxide separation and capture: A review," *J. Environ. Sci.*, vol. 20, no. 1, pp. 14–27, 2008.

[2] E. A. Jaseer, M. N. Akhtar, M. Osman, A. Al-Shammari, H. B. Oladipo, K. Garcés, F. J. Fernández-Alvarez, S. Al-Khattaf, and L. A. Oro, "Solvent-free iridium-catalyzed CO_2 hydrosilylation: experiments and kinetic modeling," *Catal. Sci. Technol.*, vol. 5, no. 1, pp. 274–279, 2015.

[3] K. Hideomi, K. Fumiaki, K. Hirohiko, and H. Hidefumi, "Hydrosilylation of carbon dioxide catalysed by ruthenium complexes," pp. 213–214, 1981.

[4] S. Park, D. Be, and M. Brookhart, "An Efficient Iridium Catalyst for Reduction of Carbon Dioxide to Methane with Trialkylsilanes," no. eq 1, pp. 10–13, 2012.

[5] T. Matsuo and H. Kawaguchi, "From Carbon Dioxide to Methane: Homogeneous Reduction of Carbon Dioxide with Hydrosilanes Catalyzed by Zirconium-Borane Complexes," no. entry 4, pp. 12362–12363, 2006.

[6] F. Gassner, E. Dinjus, H. Görls, and W. Leitner, "Formation of the Catalytically Active Intermediate in the Hydrogenation of Carbon Dioxide to Formic Acid Using the $[\{(COD)Rh(\mu\text{-}H)\}_4]/Ph_2P(CH_2)_4PPh_2$ Catalyst: First Direct Observation of Hydride Migration from Rhodium to Coor," *Organometallics*, vol. 15, no. 8, pp. 2078–2082, 1996.

[7] O. Jacquet, X. Frogneux, C. Das Neves Gomes, and T. Cantat, "CO_2 as a C1-building block for the catalytic methylation of amines," *Chem. Sci.*, vol. 4, no. 5, p. 2127, 2013.

[8] P. Haynes, L. H. Slaugh, and J. F. Kohnle, "Formamides From Carbon Dioxide, Amines and Hydrogen in the Presence of Metal Complexes," *Tetrahedron Lett.*, vol. 5, no. 5, pp. 365–368, 1970.

[9] F. J. Fernández-Alvarez, A. M. Aitani, and L. A. Oro, "Homogeneous catalytic reduction of CO_2 with hydrosilanes," *Catal. Sci. Technol.*, vol. 4, no. 3, p. 611, 2014.

[10] A. Berkefeld, W. E. Piers, and M. Parvez, "Tandem frustrated lewis pair/tris(pentafluorophenyl)borane-catalyzed deoxygenative hydrosilylation of carbon dioxide," *J. Am. Chem. Soc.*, vol. 132, no. 31, pp. 10660–10661, 2010.

[11] S. N. Riduan, Y. Zhang, and J. Y. Ying, "Conversion of Carbon Dioxide into Methanol with Silanes over N-Heterocyclic Carbene Catalysts," *Angew. Chemie*, vol. 121, no. 18, pp. 3372–3375, Apr. 2009.

[12] G. Süss-Fink and J. Reiner, "Anionische ruthenium cluster als katalysatoren bei der hydrosilylierung von kohlendioxid," *J. Organomet. Chem.*, vol. 221, no. 3, pp. C36–C38, 1981.

[13] A. Jansen and H. Go, "trans - $[Ru(II)Cl(MeCN)_5][Ru(III)Cl_4(MeCN)_2]$: A Reactive Intermediate in the Homogeneous Catalyzed Hydrosilylation of Carbon Dioxide," vol. 4, no. 8, pp. 135–138, 2000.

[14] L. Zhang, J. Cheng, and Z. Hou, “Highly efficient catalytic hydrosilylation of carbon dioxide by an N-heterocyclic carbene copper catalyst,” *Chem. Commun.*, vol. 49, no. 42, p. 4782, 2013.

[15] S. Itagaki, K. Yamaguchi, and N. Mizuno, “Catalytic synthesis of silyl formates with 1atm of CO_2 and their utilization for synthesis of formyl compounds and formic acid,” *J. Mol. Catal. A Chem.*, vol. 366, pp. 347–352, 2013.

[16] T. C. Eisenschmid and R. Eisenberg, “*Organometallics* 1989, 8, 1822-1824,” no. d, pp. 1822–1824, 1989.

[17] R. Lalrempuia, M. Iglesias, V. Polo, P. J. Sanz Miguel, F. J. Fernández-Alvarez, J. J. Pérez-Torrente, and L. A. Oro, “Effective Fixation of CO_2 by Iridium-Catalyzed Hydrosilylation,” *Angew. Chemie Int. Ed.*, vol. 51, no. 51, pp. 12824–12827, 2012.

[18] K. Motokura, D. Kashiwame, A. Miyaji, and T. Baba, “Copper-Catalyzed Formic Acid Synthesis from CO_2 with Hydrosilanes and H_2O.,” *Org. Lett.*, no. 4, pp. 1–4, 2012.

[19] Y. Nitta, O. Suwata, Y. Ikeda, Y. Okamoto, and T. Imanaka, “Copper-zirconia catalysts for methanol synthesis from carbon dioxide: Effect of ZnO addition to Cu-ZrO_2 catalysts,” *Catal. Letters*, vol. 26, pp. 345–354, 1994.

[20] I. a Fisher, H. C. Woo, and a T. Bell, “Effects of zirconia promotion on the activity of Cu/SiO_2 for methanol synthesis from CO/H_2 and CO_2/H_2,” *Catal. Letters*, vol. 44, pp. 11–17, 1997.

[21] C. Das Neves Gomes, E. Blondiaux, P. Thuéry, and T. Cantat,

"Metal-Free Reduction of CO_2 with Hydroboranes: Two Efficient Pathways at Play for the Reduction of CO_2 to Methanol," *Chem. A Eur. J.*, vol. 20, no. 23, pp. 7098–7106, 2014.

[22] J. M. Lehn and R. Ziessel, "Photochemical generation of carbon monoxide and hydrogen by reduction of carbon dioxide and water under visible light irradiation.," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 79, no. 2, pp. 701–704, 1982.

[23] S. Ichikawa and R. Doi, "Hydrogen production from water and conversion of carbon dioxide to useful chemicals by room temperature photoelectrocatalysis," *Catal. Today*, vol. 27, pp. 271–277, 1996.

[24] G. Kishan, M. Lee, S. Nam, M. Choi, and K. Lee, "The catalytic conversion of CO_2 to hydrocarbons over Fe – K supported on Al_2O_3 – MgO mixed oxides," *Catal. Letters*, vol. 56, pp. 215–219, 1998.

[25] S.-S. Nam, H. Kim, G. Kishan, M.-J. Choi, and K.-W. Lee, "Catalytic conversion of carbon dioxide into hydrocarbons over iron supported on alkali ion-exchanged Y-zeolite catalysts," *Appl. Catal. A Gen.*, vol. 179, no. 1–2, pp. 155–163, 1999.

[26] M. Honda, M. Tamura, Y. Nakagawa, S. Sonehara, K. Suzuki, K. I. Fujimoto, and K. Tomishige, "Ceria-catalyzed conversion of carbon dioxide into dimethyl carbonate with 2-cyanopyridine," *ChemSusChem*, vol. 6, pp. 1341–1344, 2013.

[27] S. Wada, K. Oka, K. Watanabe, and Y. Izumi, "Catalytic conversion of carbon dioxide into dimethyl carbonate using

reduced copper-cerium oxide catalysts as low as 353 K and 1.3 MPa and the reaction mechanism.," *Front. Chem.*, vol. 1, no. June, p. 8, 2013.

[28] S. Chakraborty, J. Zhang, J. a Krause, and H. Guan, "An efficient nickel catalyst for the reduction of carbon dioxide with a borane.," *J. Am. Chem. Soc.*, vol. 132, no. 26, pp. 8872–3, Jul. 2010.

[29] G. Robert, D and J. Haris, D, "Char Gasification of O_2, CO_2 and H_2O: Effects of Pressure on Intrisic Reaction Kinetics," *Energy Fuels*, vol. 14, pp. 483–489, 2000.

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